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U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE

ATTORNEY'S DOCKET NUMBER

**TRANSMITTAL LETTER TO THE UNITED STATES
DESIGNATED/ELECTED OFFICE (DO/EO/US)
CONCERNING A FILING UNDER 35 U.S.C. §371**

MERCK 2395

U.S. APPLICATION NO. (If known, see 37 CFR §1.5)

10/070000

INTERNATIONAL APPLICATION NO.

PCT/EP00/08312

INTERNATIONAL FILING DATE

25 AUGUST 2000

PRIORITY DATE CLAIMED

1 SEPTEMBER 1999

TITLE OF INVENTION

ELECTROPLATING SOLUTION FOR COPPER ELECTROPLATING

APPLICANT(S) FOR DO/EO/US


HU, Jung-Chih, et al.

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. §371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. §371.
3. ☐ This express request to begin national examination procedures (35 U.S.C. §371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. §371(b) and PCT Articles 22 and 39(1).
4. ☒ A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. ☒ A copy of the International Application as filed (35 U.S.C. §371(c)(2))
 - a. ☐ is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☒ has been transmitted by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ A translation of the International Application into English (35 U.S.C. §371(c)(2)).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. §371(c)(3))
 - a. ☐ are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. ☐ have been transmitted by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. §371(c)(3)).
9. ☐ An oath or declaration of the inventor(s) (35 U.S.C. §371(c)(4)).
10. ☐ A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. §371(c)(5)).

Items 11. to 16. below concern document(s) or information included:

11. ☐ An Information Disclosure Statement under 37 C.F.R. §§1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 C.F.R. §§3.28 and 3.31 is included.
13. ☐ A **FIRST** preliminary amendment.
☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
14. ☐ A substitute specification.
15. ☐ A change of power of attorney and/or address letter.
16. ☐ Other items or information:

U.S. APPLICATION NO. (if known, see 37 CFR §1.5) 10/070000		INTERNATIONAL APPLICATION NO. PCT/EP00/08312		ATTORNEY'S DOCKET NUMBER MERCK 2395	
17. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR §1.492 (a) (1) - (5)): Search Report has been prepared by the EPO or JPO..... \$890.00 International preliminary examination fee paid to USPTO (37 CFR §1.482)..... \$710.00 No international preliminary examination fee paid to USPTO (37 CFR §1.482) but international search fee paid to USPTO (37 CFR §1.445(a)(2))..... \$740.00 Neither international preliminary examination fee (37 CFR §1.482) nor international search fee (37 CFR §1.445(a)(2)) paid to USPTO..... \$1040.00 International preliminary examination fee paid to USPTO (37 CFR §1.482) and all claims satisfied provisions of PCT Article 33(2)-(4)..... \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY	
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 C.F.R. §1.492(e)). <input type="checkbox"/> 20 <input type="checkbox"/> 30					
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	3 - 20 =	0	x \$ 18.00	\$0.00	
Independent claims	1 - 3 =	0	x \$ 84.00	\$0.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)			+ \$ 280.00		
TOTAL OF ABOVE CALCULATIONS =				\$890.00	
Reduction of 1/2 for filing by small entity, if applicable. A Verified Small Entity Statement must also be					
SUBTOTAL =				\$890.00	
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 C.F.R. §1.492(f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30					
TOTAL NATIONAL FEE =				\$890.00	
Fee for recording the enclosed assignment (37 C.F.R. §1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 C.F.R. §§3.28, 3.31). \$40.00 per property.					
TOTAL FEES ENCLOSED =				\$890.00	
				Amount to be refunded:	
				charged:	
a. <input checked="" type="checkbox"/> A check in the amount of <u>\$890.00</u> to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. <u>13-3402</u> in the amount of \$_____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>13-3402</u> . A duplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 C.F.R. §§1.494 or 1.495 has not been met, a petition to revive (37 C.F.R. §1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO: Customer Number 23,599 PATENT TRADEMARK OFFICE					
 23599			SIGNATURE <u>Anthony J. Zelano</u> NAME <u>27,969</u> REGISTRATION NUMBER		
Filed: AJZ/kmo 1 MARCH 2002					

IN THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EQ/US)

International Application No. : PCT/EP00/08312
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 Applicant(s) : HU, Jung-Chih, et al

Title: ELECTROPLATING SOLUTION FOR COPPER ELECTROPLATING

PRELIMINARY AMENDMENT

Commissioner for Patents
 Box PCT
 Washington, D.C. 20231
 Sir:

Prior to calculating the national fee, please amend the above-identified application as follows:

IN THE SPECIFICATION:

Page 27, after paragraph 8, please insert the following:

--Fig 14 Showed the images of pattern wafer before electroplating

Fig 15 The relationship of Cu film resistivity vs. various concentration of HCl (CuSO₄•5H₂O at 90 g/l, H₂SO₄ at 197 g/l, current density at 2.4 A/dm² and time at 2 min)

Fig 16 The uniformity at the top of the trench is (a) not smooth without HCl addition (b) more smooth with HCl addition

Fig 17 Voids are obviously formed in the trench without any additive agent addition

Fig 18 The relationship of Cu film resistivity vs. various concentration of (NH)₂CS.
 (CuSO₄•5H₂O at 90 g/l, H₂SO₄ at 197 g/l, HCl at 70 ppm, current density at 2.4 A/dm² and time at 2 min)

Fig 19 SEM image of the electroplated Cu film at 0.03 g/l of thiourea addition, applied current density is 2.4 A/dm².

Fig 20 SEM image of the electroplated Cu film at 0.054 g/l of thiourea addition, applied current density was 2.4 A/dm²

Fig 21 The relationship of Cu film resistivity vs. deposition time ((CuSO₄•5H₂O at 90 g/l, H₂SO₄ at 197 g/l, HCl at 70 ppm current density at 1.2 A/dm²)

Fig 22(a) SIMS analysis on Cu film without thiourea presence

Fig 22(b) SIMS analysis on Cu film with thiourea 0.0036 g/l addition--

1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62 63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86 87 88 89 90 91 92 93 94 95 96 97 98 99 100

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Electroplating solution for copper electroplating

5 The present invention concerns to a novel electroplating solution for copper electroplating. Hydroxyl amine sulfate or hydroxyl amine hydrochloride are used as additive agents and added into the electroplating solution used in copper electroplating process of semiconductor manufacturing.

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(I) Introduction

Low resistivity and expected good reliability of copper make it an obvious choice used for long and narrow interconnections. However, processing difficulties associated with Cu still need to be overcome before the introduction of Cu metallization. In addition, a commercially matured equipment still needs to be developed in order to bring Cu metallization into production.

Via and trench will be filled with copper by plating (also called electrochemical deposition). However, a major drawback of electroless copper deposition process is low plating rate. Other shortcomings, e.g. contamination, healthy, complex compounds, hard to control its composition are also to be considered. Electroplating is an attractive alternative for copper deposition, since it is not available for tungsten or aluminum. Electroplating is a very inexpensive process compared to vacuum fabrication and electroless deposition. A number of research groups have developed electroplating to use in damascene structures. A potential disadvantage of electroplating is that it is a two-step process. PVD or CVD method can be completed in one step (directly on top of the diffusion-barrier), while electroplating requires deposition of a thin seed-layer prior to the plating fill step. The seed-layer provides a low-

resistance conductor for the plating current that drives the process, and also facilitates film nucleation. If seed layer is not perfect (i.e., continuous), it can create a void during copper filling.

Copper is the most favorable material used for seed layer because of its high conductivity, and because it is an ideal nucleation layer with high conductivity. Copper seed layer plays two critical roles during electroplating. On the wafer scale, seed layer carries current from the edge of the wafer to the center, allowing plating current source to contact the wafer only near the edge. The thickness of seed layer must be sufficient large so that voltage drops from wafer edge to center does not reduce electroplating uniformity. On a localized region, seed layer carries current from the top surface to the bottom of vias and trenches. When there is insufficient seed-layer thickness at the bottom, a void is formed at the center of via or trench during deposition. In order to produce a uniform and good adhesion film of electroplated copper, a seed layer must be deposited perfectly over the barrier layer.

In principle, the thickness of the seed layer at the bottom (in a high aspect ratio feature) can be increased by increasing the thickness of copper that deposited on the field. However, an excess of seed material deposited at the field level will pinch off the via or trench, creating a

center void in the film. Although PVD copper has poor step coverage in a high-aspect-ratio of vias and trenches, it has been successfully applied to Cu electroplating. PVD copper used for seed layer is successful at the narrowest feature of $0.3 \mu\text{m}$. At the dimension below $0.3 \mu\text{m}$, PVD copper seed layer can be deposited using ionized PVD methods. In addition, a CVD seed layer will probably be used for next generations.

Copper CVD is good alternative used for seed-layer primarily because it has nearly 100% step coverage. A superior step-coverage of the CVD copper process requires no additional cost relative to the PVD process. CVD copper seed-layer process can be used to fill narrow via completely in a single-damascene application, which is a significant process in future technique.

Although electroplating is a two-step process, calculations indicate that it offers a lower overall cost-of-ownership (COO) compared to CVD. The COO calculation includes the cost of the deposition equipment, fabrication space and consumables, but neglects device or process yield. The major difference is mainly due to lower capital and chemical costs of the electroplating process. Most importantly, a well-tuned electroplating process can fill a high-aspect-ratio structures.

(III) Enhanced Gap Filling Capability in Electroplating

The big challenge in Damascene plating is to fill vias \ trenches without void or seam formations. Fig 1 presents possible evolution of plated copper. In conformal plating, a deposit of equal thickness at every point of a certain dimension leads to the creation of a seam, or voids form because of different deposition rate. Sub-conformal plating leads to the formation of a void even in straight-walled features. Sub-conformal plating is resulted from substantial depletion of the cupric ion in the plating solution inside the feature, which produces significant concentration overpotentials to cause the current to flow preferentially to more accessible locations outside the feature. In order to get defect-free filling, an increasing deposition rate along the sides and the bottom of the feature is desired. As early as 1990 at IBM, they discovered certain plating solutions that contain additives could lead to super-conformal formation that eventually produces void-free and seamless structures [Fig 1]. They call this is "super-filling".

In generally, the electroplating rate is a direct function of current density. If one has a high density at the top of a structure (or at the top sharp edges) and a lower density at the bottom, one gets a different

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plating rate. Voids form because there is faster plating on the top sharp edges of trenches compared to on the bottoms. Two methods to enhance deposition uniformity and gap filling capability in electroplating process are physical and chemical approaches.

Physical method is to apply a pulsed plating (PP) or periodic pulse reverse (PPR) with both positive and negative pulses (etc., a waveform to the cathode / anode system). Periodic pulsed plating (PPR) techniques could reduce the formation of voids because the rate of metal deposition inside a trench is nearly the same as the rate at the upper portion. It is virtually like a deposition / etching sequence. It can produce a deposition / etching sequence that polish copper in the high-density regions more quickly than in the low-density regions, and produce the required gap fill capability. Pulsed plating (PR) can decrease the effective mass transfer boundary layer thickness and thus produce higher instantaneous plating current density as well as better copper distribution. Decreasing thickness of boundary layer could lead to significant concentration overpotentials decreased. Therefore, the filling capability could be enhanced in a high aspect ratio of via / trench.

Chemical method is to add organic additives in the electroplating solution. A widely used electroplating solution consists of many additive

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groups (e.g. thiourea, acetylthiourea, naphthalene sulfonic acid). However, levelers are chemicals with amine group (e.g. tribenzylamine). Carrying agent could promote the deposition of ductile copper, while brightener and leveling agent level out non-uniform substrates during electrodeposition. In order to make electrodeposition on small dimension very well (in very high aspect ratios for future ULSI metallization), an understanding of additive agent is required to further study. Establishing proper agents in a specific action and a proper concentration ratio often determines the success of a gap filling plating process.

In 1995, Intel corporation utilized a pulsed electroplating technology in a damascene process to produce low resistance copper interconnects with aspect ratios of 2.4:1. [Fig 3a & 3b.] A tantalum barrier layer (about 300-600A thickness) and a copper seed layer were deposited using collimated PVD. Nominally the thickness of the copper seed layer was 1100A on the top of the substrate, 280A on the sidewall and 650A on the bottom of the trench. After electroplating of about 1.5-2.5 μm of copper at a rate of 500-2000 A/min, the samples were processed by chemical mechanical polishing to remove the field metallization and leave copper in the trenches and vias. The resistivity of electroplated copper was lower

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than $1.88 \mu \Omega \cdot \text{cm}$. They demonstrated that the filling capability was heavily dependent upon the sputtered copper uniformity in the trenches. If sputtered copper coverage showed a significant closure at the top of the trench, then large voids could be formed after plating. However, if a uniform copper were sputtered in the trenches, then a good copper filling would occur during plating. In addition, an inadequate waveform control could result in severe void under the identical sputtering and plating condition.

In 1998, CuTek Research Inc. developed a new deposition system, which has a standard cluster tool configuration with a fully automatic dry/clean wafer in and dry/clean wafer out operation. Cu electroplating is performed on a Cu seed layer with a thickness of 30-150nm. A sputtered Ta or TaN with 30nm thickness is used as a barrier and an adhesion layer, respectively. An excellent gap filling with thicker deposited in the trenches than on top of the field surface could be achieved using pulse plating (PP) and periodic pulse reverses (PPR) with suitable additive agents. Dual damascene structures with $0.4 \mu \text{m}$ feature size in an aspect-ratio of 5:1 and deep contact structures with $0.25 \mu \text{m}$ feature size in an aspect-ratio of 8:1 could be completely filled without any void or seam function. The impurity contained in electroplated Cu film is measured to

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be below 50ppm. The major contaminants found were H, S, Cl, and C. A higher concentration of these elements is measured at the edge of wafer in comparison with the center. This is probably due to high hydrogen evolution and higher organic additive incorporated at the high current density region.

In 1998, UMC (United Microelectronics Corporation) has demonstrated the integration of copper process by using a simple and cost-effective dual damascene architecture. The metal-filling process for Cu interconnection includes (1) a deposition of 400Å ionized-metal-plasma (IMP) Ta or TaN which serves as barrier to prevent Cu diffusion and as an adhesion promoter of Cu to oxide IMD layer, (2) a PVD Cu seed layer, and (3) a Cu electroplating. An excess of Cu over oxide is removed by using chemical-mechanical polish (CMP) technique. The optimized metal deposition process is able to fill a high aspect-ratio (~5) of a 0.28 μ m feature hole without seams formation.[Fig. 4]

(VI) Experiment

【A】 Basic

Two major components in the electroplating process are compositions of the electroplating solution and the method in which the current applied. In section (I), we have discussed how to select the method of current applied and the composition of electroplating solution. In addition, it is noticed that the electrolytic production of copper in copper deposition and the control of the cathode growth are very important. The reason is important because cathode growth is affected by many factors: (a) the quality of anode, (b) the electrolyte composition and impurities, (c) the current density. (d) The surface condition of the starter cathode, (e) the geometric anode and cathode (f) the uniformity of spacing (agitation) and the distance between electrodes and (g) the temperature or current density.

Electroplating can be carried out at a constant current, a constant voltage, or at variable waveforms of current or voltage. In our experiment, a constant current with accurate control of the mass of deposited metal is

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most easily obtained. Plating at a constant voltage with variable waveforms requires more complex equipment and control. The temperature of electroplating solution in experiment process is constant (at R.T). Therefore, we can neglect the influence of temperature on deposition rate and film quality.

【B】 Prepare Substrate and Experimental Process

P-type (001) oriented single crystal silicon wafers of 15-25 Ω -cm in 6-inch diameter were used as deposition substrates in this work. The blank wafers were first cleaned by a conventional wet cleaning process. After wet cleaning, wafers were treated with a dilute 1:50 HF solution before loading into a deposition chamber. A 50-nm-thickness of TiN and a 50-nm-thickness of Cu were deposited using conventional PVD to act as a diffusion barrier and a seed layer, respectively. Patterned wafers were fabricated to examine the ability of Cu electroplating in small trenches and vias. After standard RCA cleaning, wafers were treated with thermal oxidation. Then, a photolithography technique with reactive ion etching (RIE) was used to define a definite dimension of trenches/vias. A 40-nm-thickness of TaN used as barrier and a 150-nm-thickness of Cu used as seed layer were deposited by ionized metal plasma (IMP) PVD,

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respectively. The dimension of trench/via was defined between 0.3-0.8 μm . An electroplating solution, which was used for Cu electroplating, was usually composed of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_2SO_4 , Cl^- , additives, and wetting agent. The compositions of the electroplating solution were described in Table 2. Additives were frequently added in Cu electroplating because they worked as brightening, hardening, grain refining, and leveling agents. The current density applied was 0.1-4 A/dm^2 . Besides, Cu(P) (Cu: 99.95 %, P: 0.05 %) material was used as an anode to supply sufficient Cu ions and made good quality of Cu electroplated films.

【C】 Equipment of electroplating

The simple electroplating system was described as followed: [Fig 5]

(a) Wafer : P-type (001) oriented single crystal silicon wafers of 15-25

Ω -cm in 6"-inch diameter

(b) Power Supplier : GW1860 (固偉)

(c) PP Tank: 20cm \times 19cm \times 20.5cm

(d) Rolled Copper (Cu: 99.95%, P:0.05%) : 30 piece

Produced by Meltex Learonal Japan company

(e) Titanium anode basket : 20 cm \times 19 cm \times 2 cm

【D】 Analysis Tool*(a) Field Emission Scanning Electron Microscopy (FESEM):**HITACHI S-4000*

The morphology and step coverage were examined by using field emission scanning electron microscope (FESEM).

(b) Sheet Resistance Measurement

The resistivity of electroplated Cu film was measured by a four-point probe. The sheet resistance of the Cu films were determined using a standard equal-spaced four point probe. The spacing between equal-spaced four point probes was 1.016mm. Current was passed through the outer two probes and the potential across the inner two probes was measured. The applied current was from 0.1 to 0.5mA.

(c) X-Ray Power Diffractometer (XRPD): MAC Science, MXP18

X-ray diffractometer (XRD) was utilized to investigate crystal

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orientation of Cu electroplated films. X-ray analysis was performed in a Shimadzu diffractometer and employed with Cu K α radiation (λ = 1.542 Å) in conventional reflection geometry and scintillation counter detection.

(d) *Auger Electron Spectroscopy (AES) : FISON'S Microlab 310F*

Auger electron spectroscopy (AES) was applied to determine the stoichiometry and uniformity along the depth direction.

(e) *Secondary Ion Mass Spectrometry (SIMS) : Cameca IMS-4f*

SIMS (Secondary Ion Mass Spectrometry) was utilized to do the contamination analysis.

(VII) Results and Discussions

【A】 The effect of applied current and concentration

In our study, we first change the concentration of sulfate acid and keep concentration of copper sulfate at constant. Fig. 6 shows the concentration change of sulfate acid vs. thickness variation. We can find no obvious change in thickness when increasing the concentration of sulfate acid. Fig. 7 presents the relationship between film resistivity and concentration of H_2SO_4 . The resistivity is constant when concentration is increasing. In Fig 8(a) & 8 (b), SEM images show film morphology with and without H_2SO_4 presence. We can find the uniformity and roughness of copper film is smoother when the sulfate acid is present and makes the resistivity of copper film lower. In our opinion, the purpose of sulfuric acid is to prevent anode polarization and to improve conductivity of the electrolyte and cathode film, but does not very strong affect on the deposited copper film.

In experiment, we keep concentrations of sulfate acid ($\approx 197\text{g/l}$) and sulfate copper (90g/l) constant. Since conductivity of solutions is higher, and anode and cathode polarization are small, voltage required for Cu deposition is small. Change in sulfate acid concentration has more influence than

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changes in copper sulfate concentration in solution conductivity and anode and cathode polarization. Fig. 9 shows the relation between applied current change and Cu deposition rates. It is found that deposition rate increases with increasing applied current. The deposition rate reaches a maximum when applied current increase to 3.2 A/dm^2 . As shown in Fig 10, we can see the resistivity changes with different applied current. When applied current is at 3.2 A/dm^2 , the resistivity become very large. Figs.11(a) and 11(b) present film morphology of Cu electroplated on seed layer / TiN / Si at various current densities ($1-4 \text{ A/dm}^2$) without additive addition. Large grain of Cu film is observed at high current density. The resistivity exhibits unusually high ($\sim 10 \mu \text{ m-cm}$) when high current is applied. A high resistivity of Cu film observed could be attribute to rough surface formation, which resulted in film non-conformity at high current condition. The rough surface formed at high current could be rationalized by following postulations. It was supposed that Cu electroplating rate depended on Cu ions diffusion onto substrate surface. At high current applied, most of Cu ions were effected at a high electric field; therefore, Cu ions diffusion from solution to substrate surface was very fast. Since Cu ion diffusions was very fast, the depletion of Cu ions in diffusion layer was very rapid; Cu ions could not be supplied instantly from electroplated solution into diffusion

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layer. The Cu electroplating was limited by Cu ion diffusion. This was called diffusion controlled. Since no replenish of Cu ions diffused onto substrate surface, no more of nucleation was formed on the surface. Cu aggregation could occur on the surface due to high electric field effect. A rough surface formed was ascribed to Cu agglomeration. Fig.12 present relative intensity ratio of Cu(111)/Cu(002) by X-ray diffraction measurement at various applied current density. According to XRD results, a strong (111) orientation was always observed at higher current density applied. The development of growth orientation of the copper film could be rationalized by considering surface energy and strain energy at different crystal orientation. In the initial stage, the orientation of Cu (002) plane was formed because this plane possessed the lowest surface energy. As applied electrical current was increased, the strain energy becomes a dominant factor in governing grain growth. The peak intensity of Cu (111) was increasing at high electrical current applied because of high strain energy in Cu (111) orientation. In addition, a Cu (111) orientation was preferred because this orientation showed better electromigration resistance. Contradictory, Cu (111) formed at high current density could make surface more roughness as shown in Fig.16 (b). In order to improve the filling of Cu electroplating, it was attempted to add some additives in electroplating solution. A high

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resistivity of Cu film at high current was also analyzed by SIMS and compared with that at low current condition (see Fig.13 a & b). The oxygen concentration in the high resistivity of Cu film is higher because of its rough surface with film non-conformity at high current condition.

【B】 The Effect of Traditional Additive Agents

In order to understand the gap filling capability in electroplating processing. Then, the dimension of trench/via was defined between 0.3-0.8 μm used to test gap filling capability. Fig. 14 shows the images of pattern wafer before electroplating. The thickness of Cu seed layer on the bottom and on the side-wall is less than on the top.

We used HCl as additive agent for electroplating. Addition of HCl does not make any prominent difference in film resistivity and film morphology in blanket wafer.[Fig.15] As shown from in pattern wafers [see Fig. 16 (a) and (b)], we find the uniformity at the top of the trench is smoother when the HCl was added in solution. Fig. 17 revealed that voids are formed if no additive agent was added into the solution.

Various organic and inorganic additives are added in solution to help Cu

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electroplating. Thiourea is a common additive, which usually added in electroplating solution. As presented in Fig. 18, the resistivity of electroplated Cu films does not show big difference when the concentration of Thiourea is smaller than 0.054 g/l. A high resistivity is observed when Thiourea is more than 0.054 g/l. Fig. 19 presents the SEM image of Cu (111) at 0.03 g/l of Thiourea addition. The current is applied at 2.4 A/dm². As shown from SEM image, addition of additives could help (111) formation at low current density, because the additive could be incorporated into the deposit to provide a specific growth orientation. Fig. 20 presents the SEM image of the electroplated Cu film at 0.054 g/l of Thiourea addition. The current applied is still to keep at 2.4 A/dm². As shown in Fig 20, when concentration of Thiourea is increasing, the dendrite produced during Cu electroplating is increasing. This dendrite has similar geometric structure with diffusion-limited clusters. Moreover, Thiourea could decompose to form pernicious product (NH₄SCN) which results in embattlement of electroplated Cu films. Fig. 21 shows the resistivity of copper film change with deposition time. It is appeared that resistivity is lower when the copper film become large block. Because that the grain boundary of copper film is decreasing to make surface more smooth than initial thin film. The resistivity of Cu film is higher when Thiourea is added. According to

SIMS results [Fig. 22(a)(b)(c)], we can find the concentration of S element is increased with increasing concentration of Thiourea. It is suggested that Thiourea adsorbed on the surface of cathode could make the resistivity of Cu increasing. In addition, voids is formed when Thiourea is used as additive agent.

PEG (polyethylene glycol) is widely used in Cu electroplating as a carrier agent. In this study, we use different molecular weight of PEG (200~10,000) and added in electrolyte with HCl and small amount of Thiourea (0.0036g/l), since small amount Thiourea could help (111) plan formation. We can found the larger molecular weight (m.w.>200) make the higher resistivity of copper film. According to Fig. 23, the resistivity of copper film is increasing with PEG molecular weight higher with deposition time. It is suggested that the longer chain length with Thiourea is absorbed on the surface of substrate. From SEM image shown in Fig.24(a)(b), film morphology doesn't change a lot when PEG molecular weight is increasing, but the plane (111) is decreasing when PEG molecular weight is increasing.[Fig. 25] According to SIMS analysis [shown in Fig.26(a)(b)], the major components of Cu film are still Cu , O, C, S and Ti. The amount of S element will be increasing with increasing molecular weight of PEG. This

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observation is proved by our suggestion which discussed previously.

Based on our results, a lot of Thiourea and larger molecular weight of PEG (m.w >200) could not be used as additives in Cu electroplating for future Cu interconnect because of higher resistivity of copper film and poor cap-filling ability. In order to make Cu electroplating implemented in ULSI processing, a suitable additive must be developed. In this study, we try new traditional additive agents of Molasses which shows the same effect on resistivity of copper film.

Glucose is also a common traditional additive agent used in Cu electroplating. In our experiment, we found the resistivity and orientation of electroplated copper film do not obvious change with different amount of Glucose. However, filling capability in via and trench is poor. Although an equal thickness at all points of a feature is formed, a void still appears in the trench.

【C】 The Effect of New Additive Agents

Sulfamates have been studied in interaction with a number of metals.

NDL

They show little tendency to form complex ions or affect the deposition by adsorption or bridging effects. Sulfamates could be used as a gap-filling promoter in Cu electroplating because it could decrease current efficient in Cu deposition. Since hydroxyl amine sulfate $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$ has a similar functional group with sulfamate, it is postulated that it could be act as a good gap filling promoter. In order to examine if hydroxyl amine sulfate could act as a gap filling promoter, Cu electroplating with addition of hydroxyl amine sulfate is investigated in this experiment. The experiment is executed on the substrates with 0.3-0.8 μm width of trench/via. Since the thickness of base layer (seed layer and diffusion barrier) is 60nm on the bottom and on the side wall and 120nm on the top, the width less than 0.25 μm could be electrodeposited in the 0.35 μm width of trench. Fig. 27 reveals void is formed if no additive is added into the solution. The dimension of trench in Fig. 31 is measured to be 0.4 μm . Since Cu reduction is preferred to occur at the region of high current (at the top of trench), a void is easy to form. No void formation is observed when the additive of $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$ is added into the electroplating solution, as shown in Fig. 28. The dimension of trench is measured to be 0.3 μm . A complete picture of SEM image in low magnification of Cu electroplated on 0.3-0.8 μm of

NDL

trench/via is presented in Fig. 29. According to previous results, it is demonstrated that Cu could be electroplated into fine trenches or small sizes of vias when hydroxyl amine sulfate is used as a gap filling promoter. In addition, the resistivity of Cu film does not show significant change. [see Fig 30] The concentration of O in the Cu film measured to be very low [Fig.31]. Therefore, oxidation of Cu or seed layer could be neglected. According to SIMS analysis, it is found that the concentration of impurity (S element) is very low in copper film [Fig.32]. A further study of this new additive is still investigated in progress.

Since hydroxyl amine sulfate $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$ has both amino and sulfate functional group, it is proposed to use as a gap filling promoter in helping Cu electroplating. Another additive agent, hydroxyl amine hydrochloride $(\text{NH}_2\text{OH}) \cdot \text{HCl}$, could be considered to use for Cu electroplating because it has a similar amine functional group with chloride. In our experiment, we use different amount of hydroxyl amine hydrochloride $(\text{NH}_2\text{OH}) \cdot \text{HCl}$ as a gap filling promoter. The ability of filling is not really good. Some trenches can be completely filled by Cu but others can not. However, the lower resistivity of copper film could be decreased to $1.9 \mu \Omega \cdot \text{cm}$ when small of hydroxyl amine hydrochloride is used in the

NDL

electrolyte compared to the Cu film with no additive added. [Fig. 30]

Another organic additives with unsaturated π -bands, like Tribenzylamine, benzotriazole and naphthalene sulfonic acid, could be considered to be use as additives in Cu electroplating. Since they have unsaturated π -bands, the π electrons could interact with surface atoms of copper, to produce substantial effect on the properties of deposits. Brightness, leveling, as well as stability effect is still needed to do further study. This study, we try to use Tribenzylamine and benzotriazole as leveling agents. However, these levels agents are quite difficult in soluble in sulfate acid solution to make experiment unworkable.

(VII) Conclusions

A strong Cu (111) peak was observed at higher electrical current applied. The development of growth orientation of the copper film could be rationalized by considering surface energy and strain energy at different crystal planes. In the initial stage, the orientation of Cu (002) plane was existed because this plane possessed the lowest surface energy. As applied electrical current was increased, the strain energy becomes a dominant factor in governing grain growth. A strong peak of Cu (111) was appeared when applied electrical current was increasing. In addition, additives played an important role in controlling the orientation of electroplated Cu films at low current density. No void formation was observed when Cu electrodeposited onto a 0.3 μm width of trench in the presence of $((\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4)$ additive. The concentration of O in the sample was measured to be rather low. Therefore, oxidation of Cu or seed layer could be neglected. In summary, sulfamate group showed little tendency to form complex ions, therefore, it could stabilize Cu (I) and reduce current efficiency for copper deposition. Since hydroxyl amine sulfate $((\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4)$ had both amino and sulfate functional groups, which were similar to sulfamate, it was postulated that hydroxyl amine sulfate could be used as a gap filling promoter in helping Cu electroplating.

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Table 1. Chemical composition of the electroplated Cu solution

Composition	Concentration
CuSO ₄ 5H ₂ O	60-150 g/l
H ₂ SO ₄	80-150 g/l
Cl ions	50-150 ppm
PEG	~100ppm
Addition agents	Small

Table Captions

Table 1. Chemical composition of the electroplated Cu solution

Figure Captions

Fig 1. Typical deposition profile in plating.

Fig 2. Schematic cross-section shows micro-roughness at cathode. The leveling is accumulated at peak (P) because diffusion is relatively fast at the short distance from the diffusion boundary. Diffusion at valley (V) is too slow to keep up with consumption of leveling agent. Consequently, metal deposition is inhibited at peak but not in the valleys, and filling in the valleys produces a smoother surface.

Fig 3.(a) Copper electroplated into a 0.4 micron trench with aspect ratio = 2.1:1

Fig 3.(b) Copper electroplated into a 0.35 micron trench with aspect ratio = 2.4:1

Fig 4. The optimized deposition process is able to fill a high aspect-ratio (~5) feature hole of a 0.28 μm via size without obvious seam formation.

Fig 5. Schematic of the Cu electroplating system.

Fig 6. Dependence of the thickness vs. H_2SO_4 concentration change.

($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at 90g/l, current density at 2.4A/dm² and time at 2min)

Fig 7. Cu films resistivity change as a function of concentration of H_2SO_4

($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at 90g/l, current density at 2.4A/dm² and time at 2min)

Fig 8. SEM images of copper film morphology with and without H_2SO_4

presence. (a) only $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (90g/l) (b) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (90g/l) & H_2SO_4 (20ml/l)

Fig 9. Dependence of film deposition rate vs. current density variation.

($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at 90g/l, H_2SO_4 at 197g/l and time at 2min)

Fig 10. Film resistivity change as a function of applied current variation.

($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at 90g/l, H_2SO_4 at 197g/l and time at 2min)

Fig 11. Cu film morphology at different applied currents..

Fig 12. XRD measurement at various applied current.

($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at 90g/l, H_2SO_4 at 197g/l and time at 2min)

Fig 13.(a) The SIMS results showed that oxygen concentration in

electroplated Cu film at low applied current density of 1.2A/dm².

Fig 13.(b) The SIMS results showed that oxygen concentration in

electroplated Cu film at high applied current density of 3.2A/dm².

Fig 22. (c) SIMS analysis on Cu film with thiourea 0.018g/l addition.

Fig 23. The resistivity of Cu films change with various PEG molecular weight at different deposition time. ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ at 90g/l, H_2SO_4 at 197g/l, HCl at 70 ppm, current density at 1.2 A.dm²)

Fig 24. Film morphology analysis with different amount of Thiourea
Addition (a) PEG1000 added (b) PEG10,000 added

Fig 25. XRD measurement at various PEG molecular weight..

Fig 26. (a)The SIMS analysis on Cu film with Thiourea and PEG200 addition.

Fig 26. (b)The SIMS analysis on Cu film with Thiourea and PEG4000 addition

Fig 27. The SEM image of the electroplated Cu film without additive agent addition. The dimension of trench is 0.25 μm .

Fig 28. The SEM image of the electroplated Cu film at 0.06g/l of $(\text{NH}_2\text{OH})\text{H}_2\text{SO}_4$ addition. The dimension of trench is 0.25 μm .

Fig 29. (a) & (b) A low magnification of the SEM image of Cu Electroplate on 0.3–0.8 μm of trench/via.

Fig 30. The resistivity change with different amount of additive agent at different deposition time.

Fig 31. The AES analysis of the Cu film at 0.06g/l of $(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4$ addition.

Fig 32. The SIMS analysis on Cu film at 0.06g/l of $(\text{NH}_2\text{OH})_2\text{H}_2\text{SO}_4$ addition.

CLAIMS

- 5 1. Electroplatingplating solution for copper comprising $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_2SO_4 , HCl , Polyethylenglycol (molecular weight >200), hydroxyl amine sulfate, hydroxyl amine chloride and if necessary further additives.
- 10 2. Solution according to claim 1 comprising Cl ions in a range of 50 – 150 ppm and hydroxyl amine sulfate in a range of 0,01 – 5 g/l.
3. Solution according to claim 1 comprising Cl ions in a range of 55 – 125 ppm.

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Veröffentlicht:

- Mit internationalem Recherchenbericht.
- Vor Ablauf der für Änderungen der Ansprüche geltenden
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Zur Erklärung der Zweibuchstaben-Codes, und der anderen
Abkürzungen wird auf die Erklärungen ("Guidance Notes on
Codes and Abbreviations") am Anfang jeder regulären Ausgabe
der PCT-Gazette verwiesen.

WO 01/16403 A1

(54) Title: GALVANIZING SOLUTION FOR THE GALVANIC DEPOSITION OF COPPER

(54) Bezeichnung: GALVANISIERUNGSLÖSUNG FÜR DIE GALVANISCHE ABSCHIEDUNG VON KUPFER

(57) Abstract: The invention relates to a novel galvanizing solution for the galvanic deposition of copper. Hydroxylamine sulfate or hydroxylamine hydrochloride are utilized as addition reagents and added to the galvanizing solution during the galvanic deposition of copper which is used in the manufacture of semiconductors.

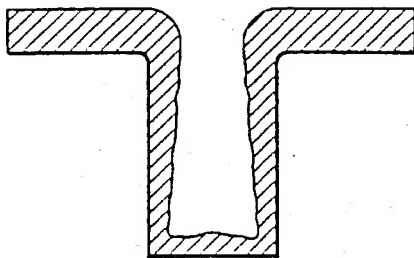
(57) Zusammenfassung: Die vorliegende Erfindung betrifft eine neue Galvanisierungslösung für die galvanische Abscheidung von Kupfer. Dabei werden Hydroxylaminsulfat und Hydroxylaminhydrochlorid als Additivreagentien verwendet und der bei der galvanischen Abscheidung von Kupfer in der Halbleiterproduktion verwendeten Galvanisierungslösung zugesetzt.

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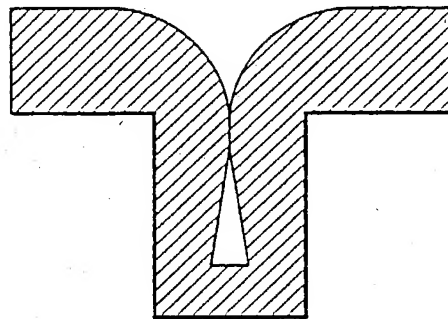
Fig. 1

Early Stages of Plating

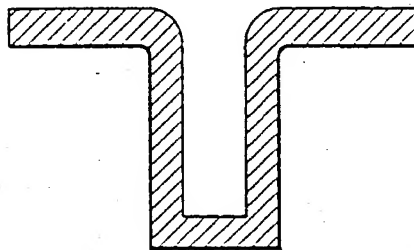
Late Stages of Plating



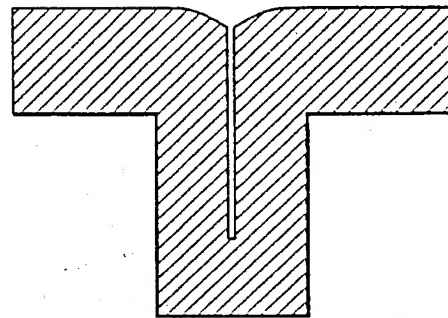
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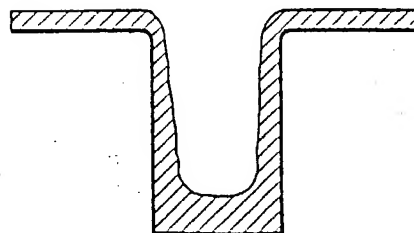
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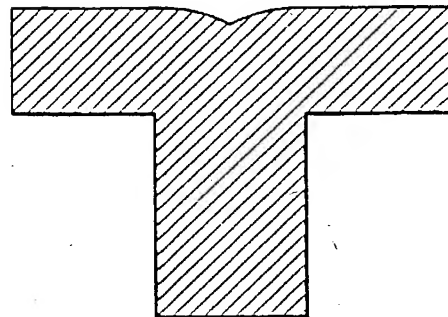
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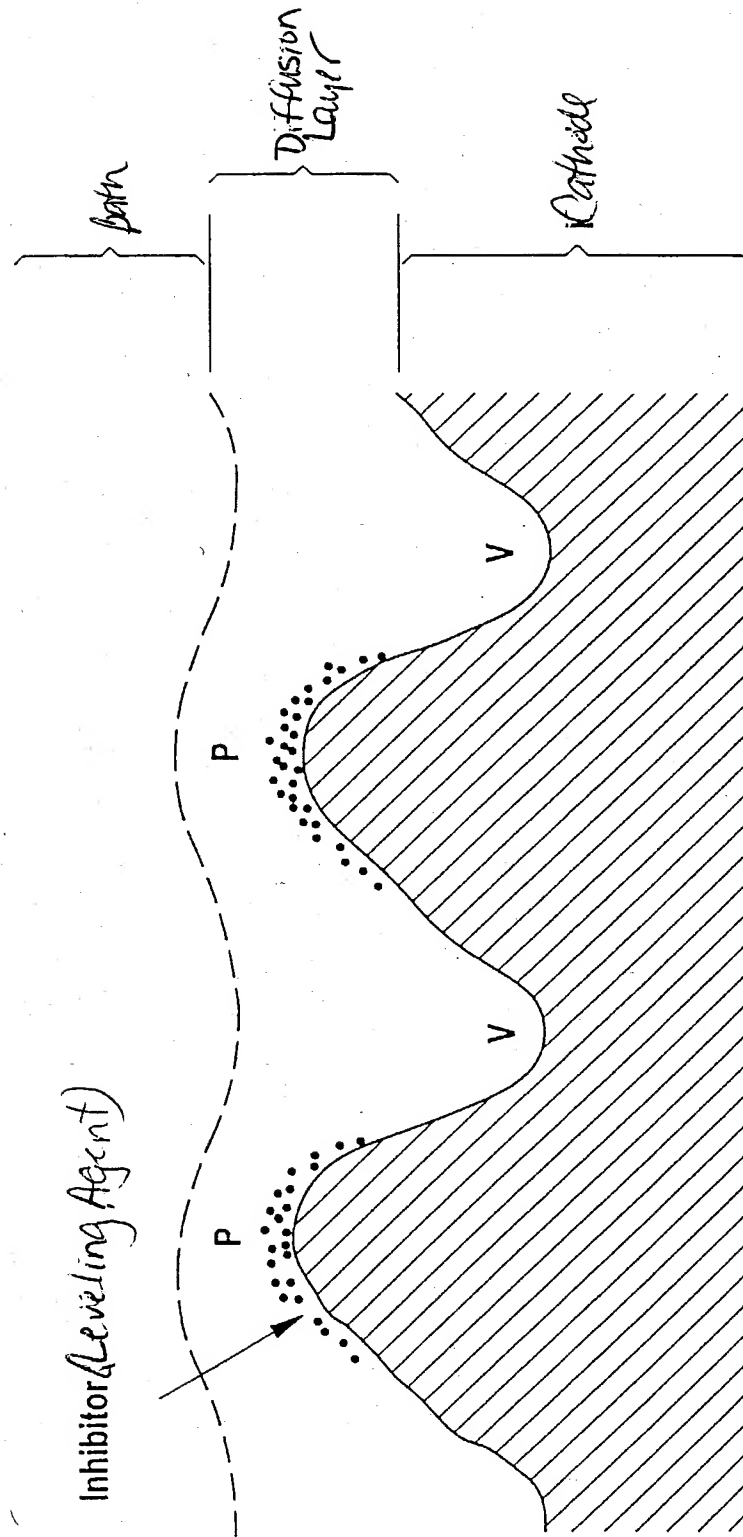
'Super-filling'



Defect-free

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Fig. 2

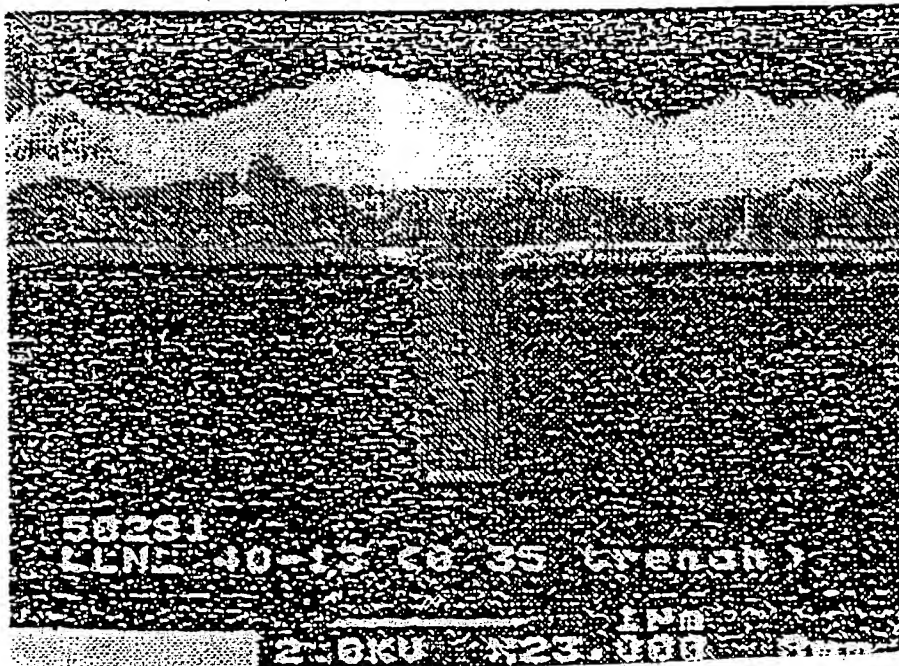


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Fig. 3a



Fig. 3b



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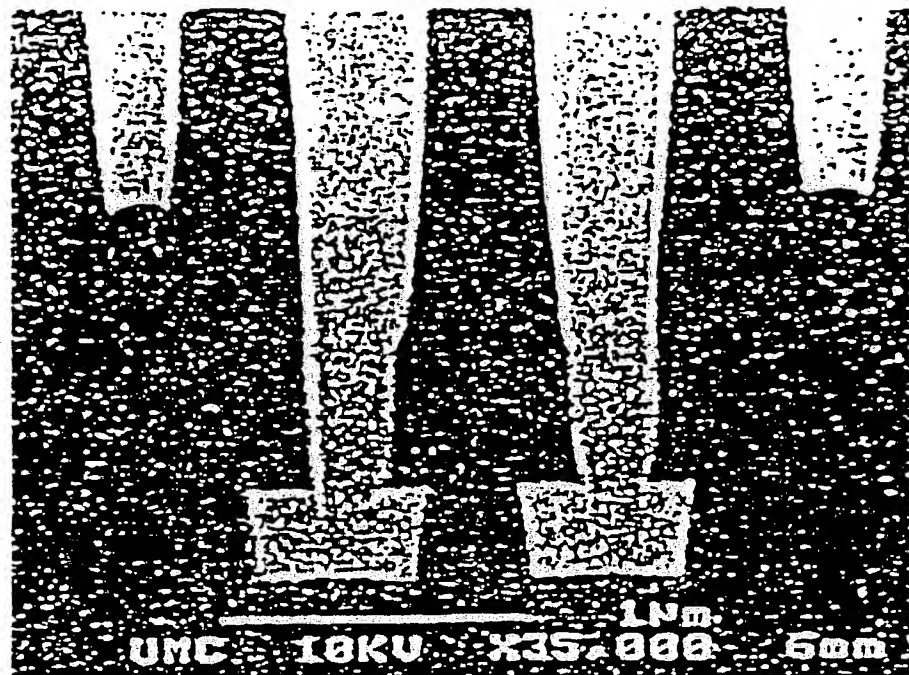
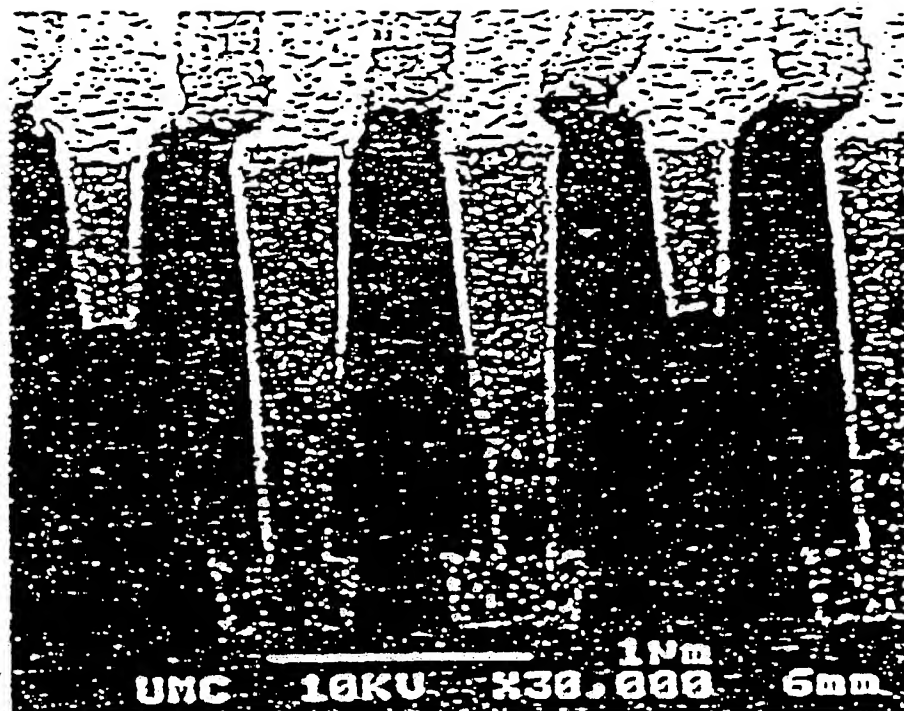


Fig. 4



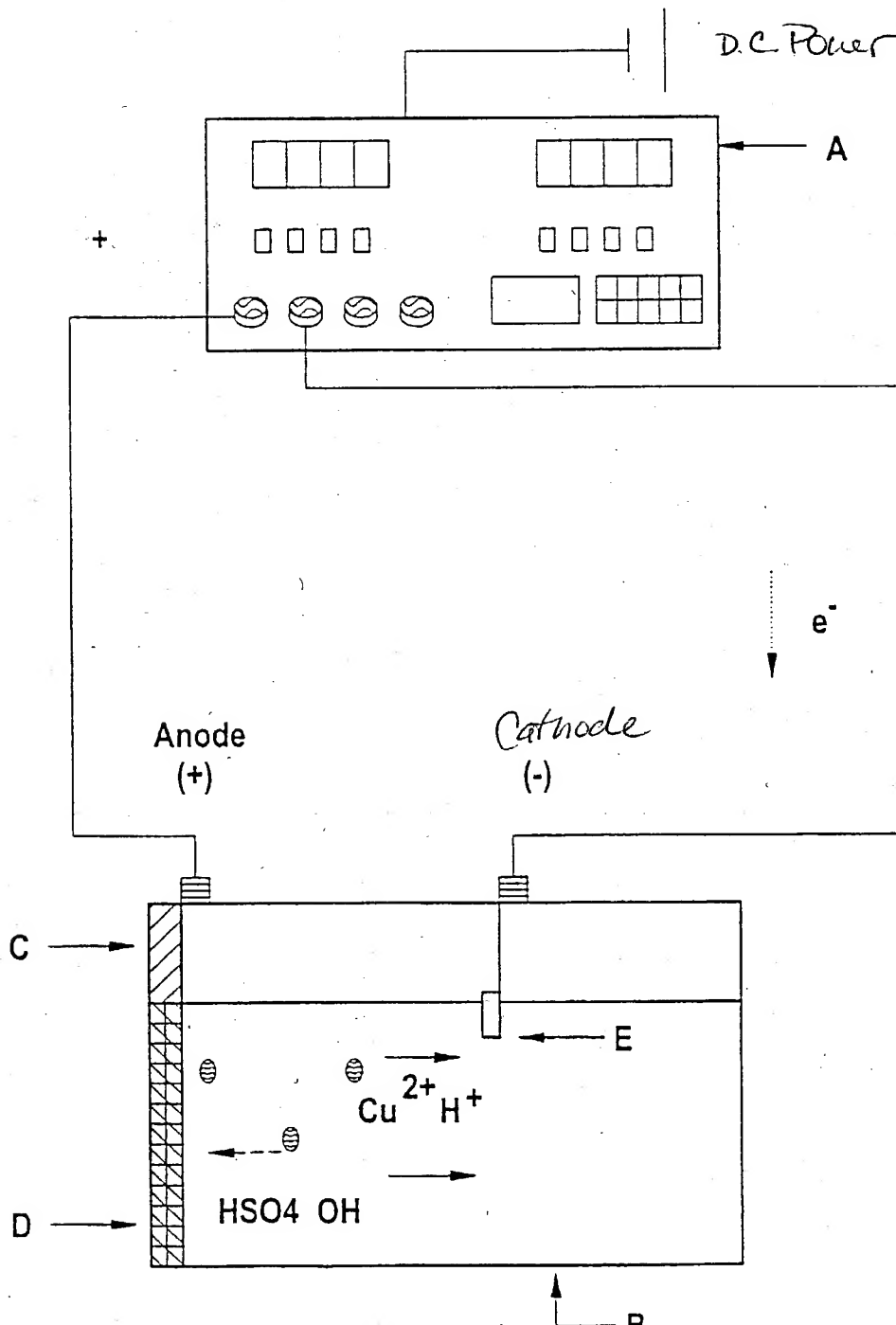
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Fig. 5

A: Power Supplied
D: Railed Copper

B: PP Tank
E: Wafer

C: Ti-Anode Basket



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Fig. 6

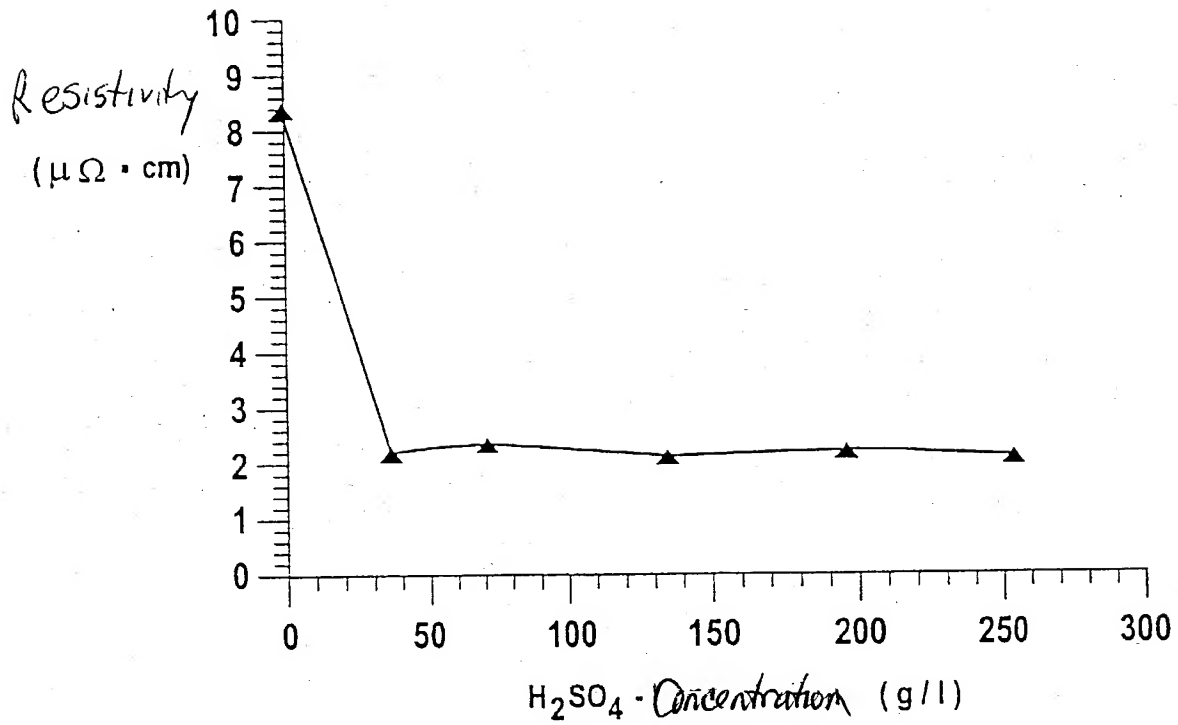
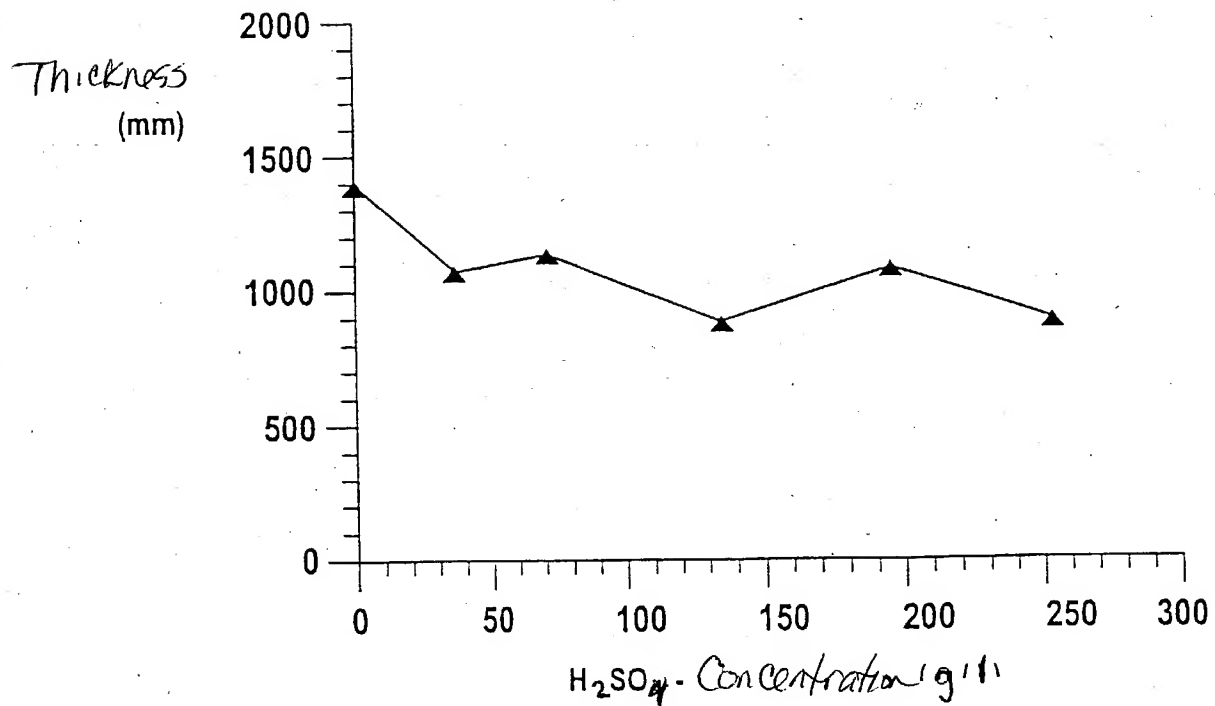


Fig. 7



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Fig. 8a

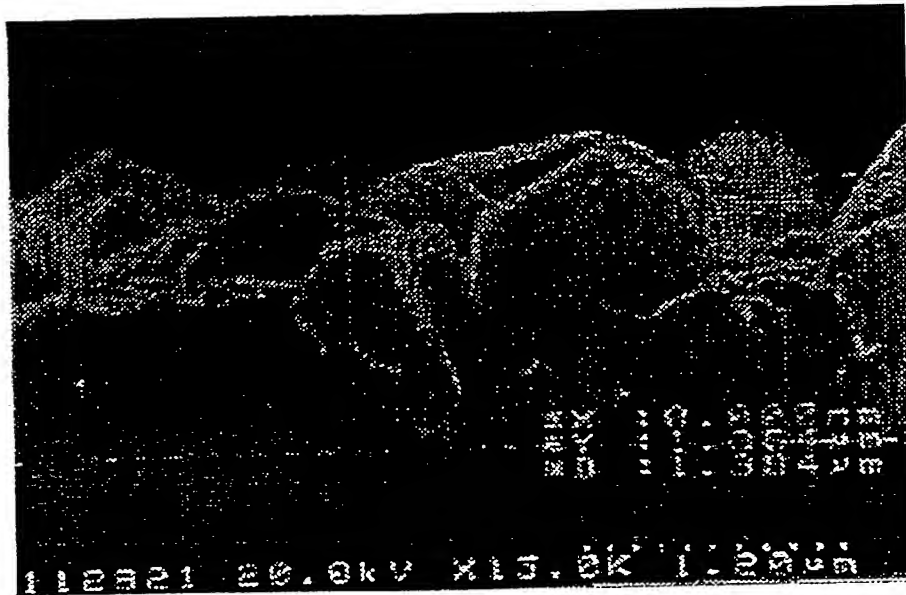
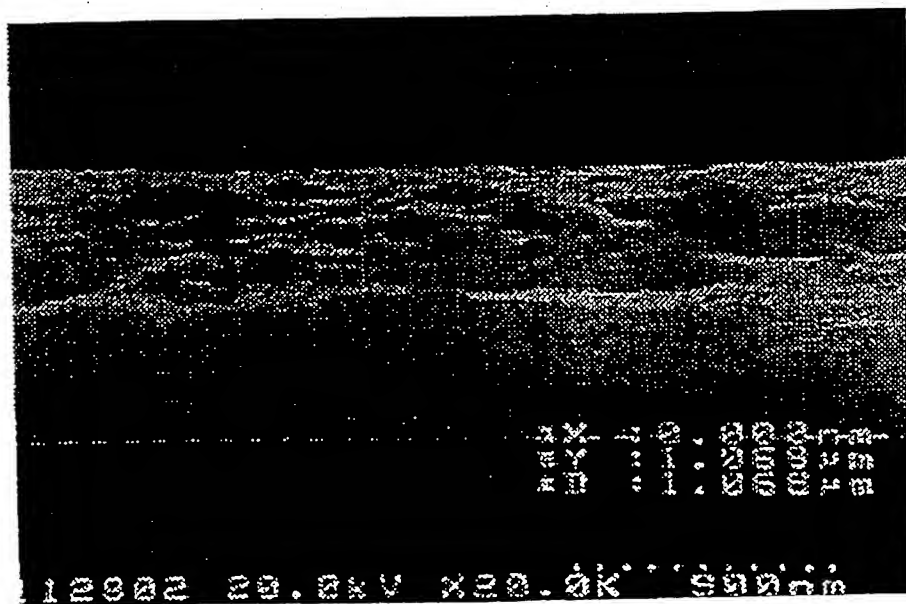


Fig. 8b



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Fig. 9

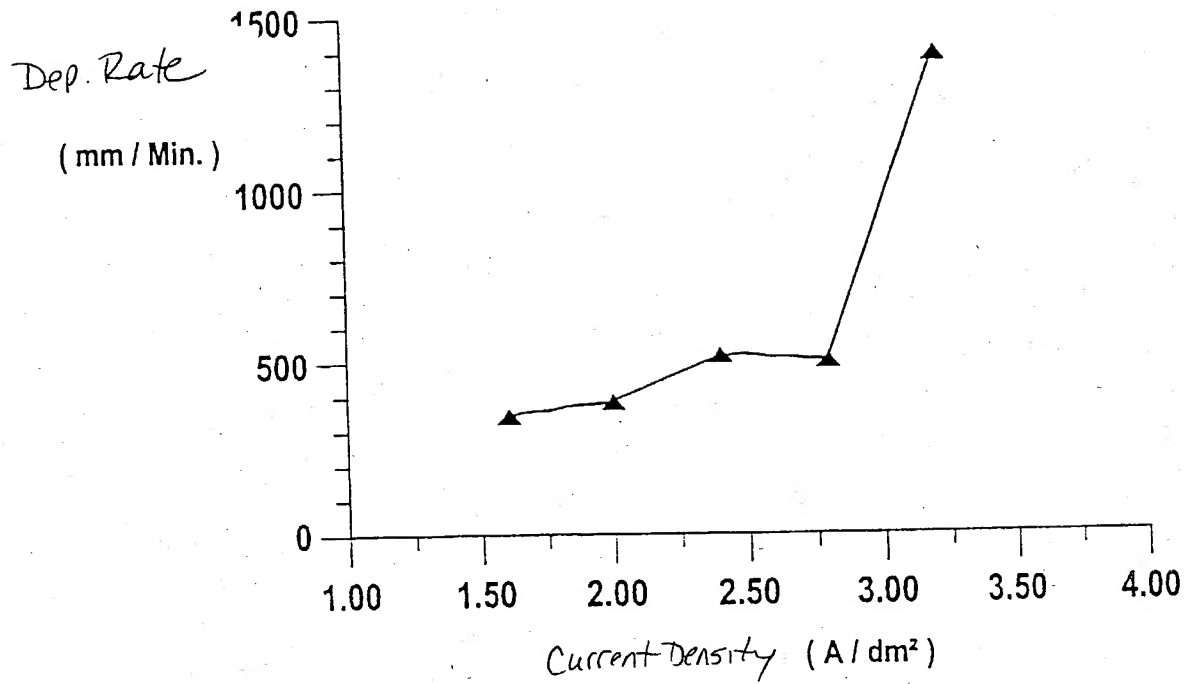
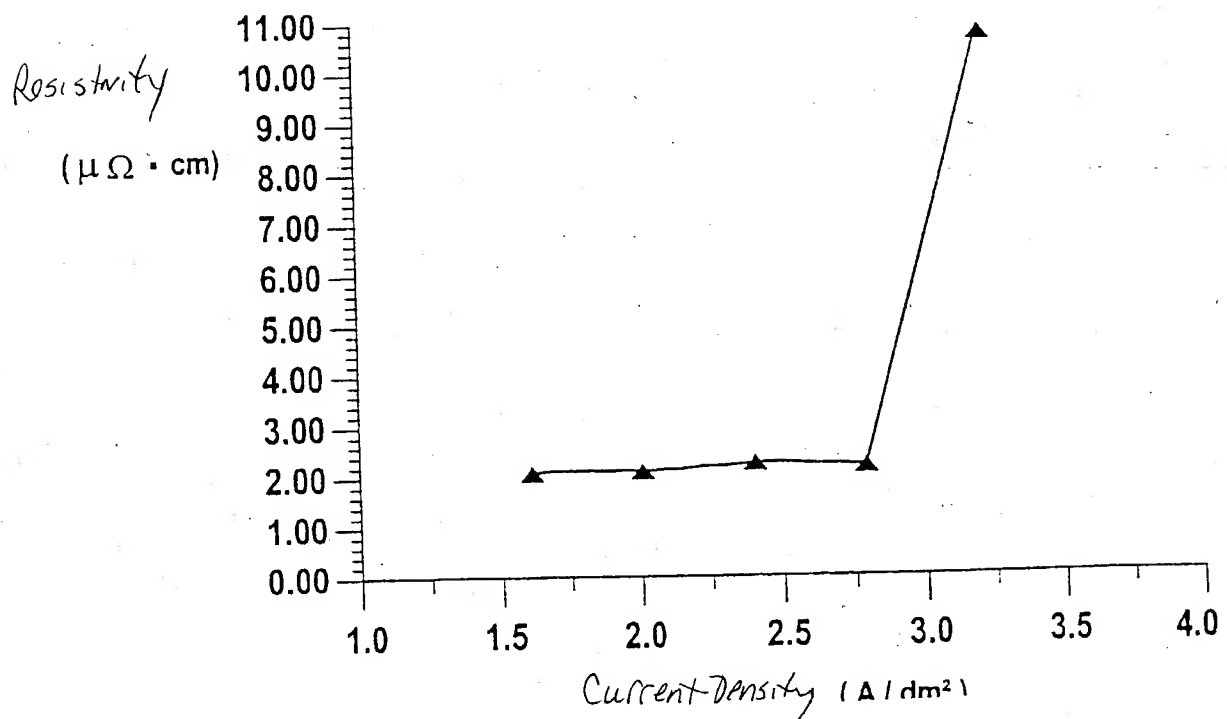


Fig. 10



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Fig. 11a

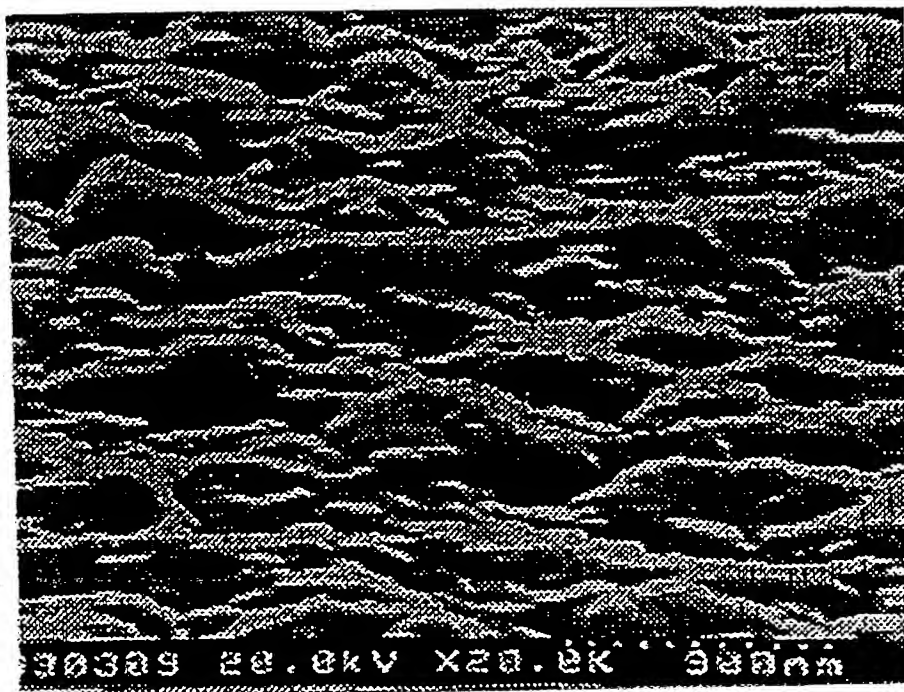
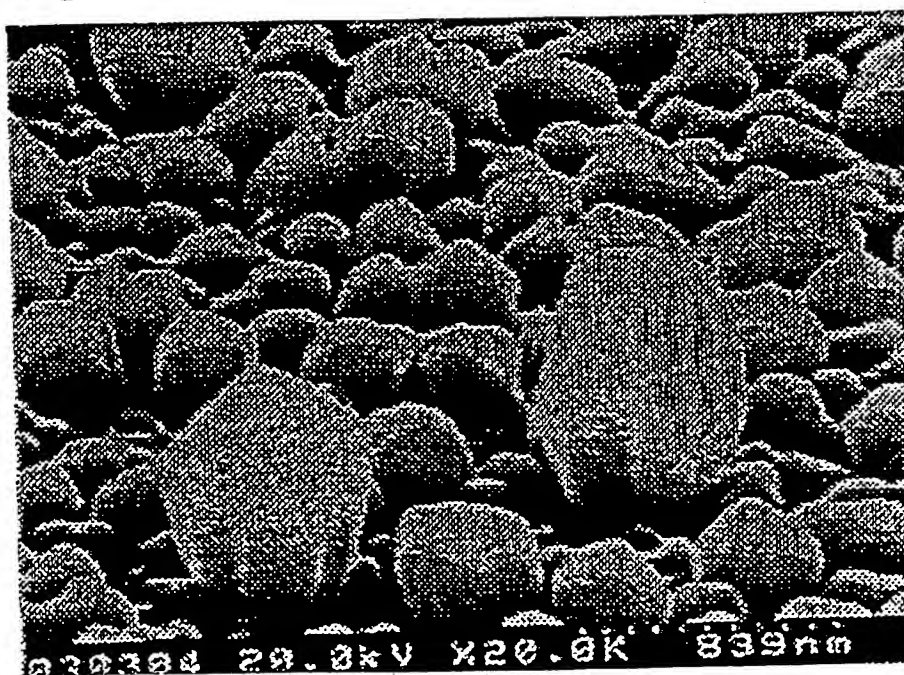
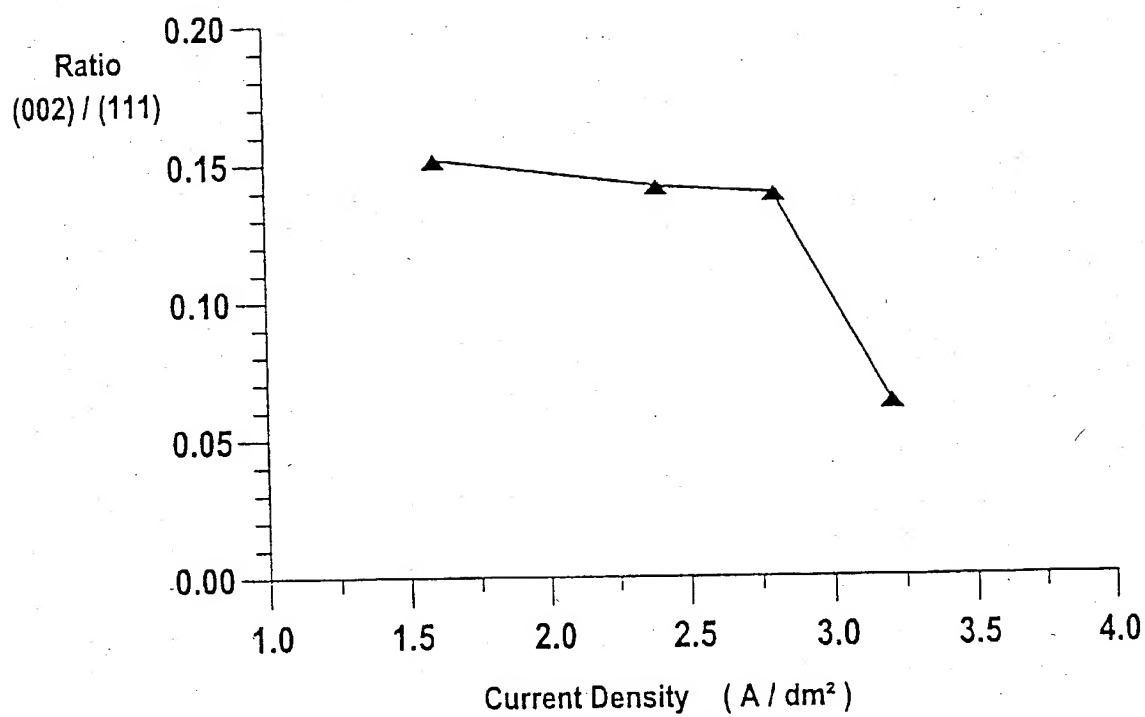
1.2 A/dm²

Fig. 11b

3.2 A/dm²

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Fig. 12

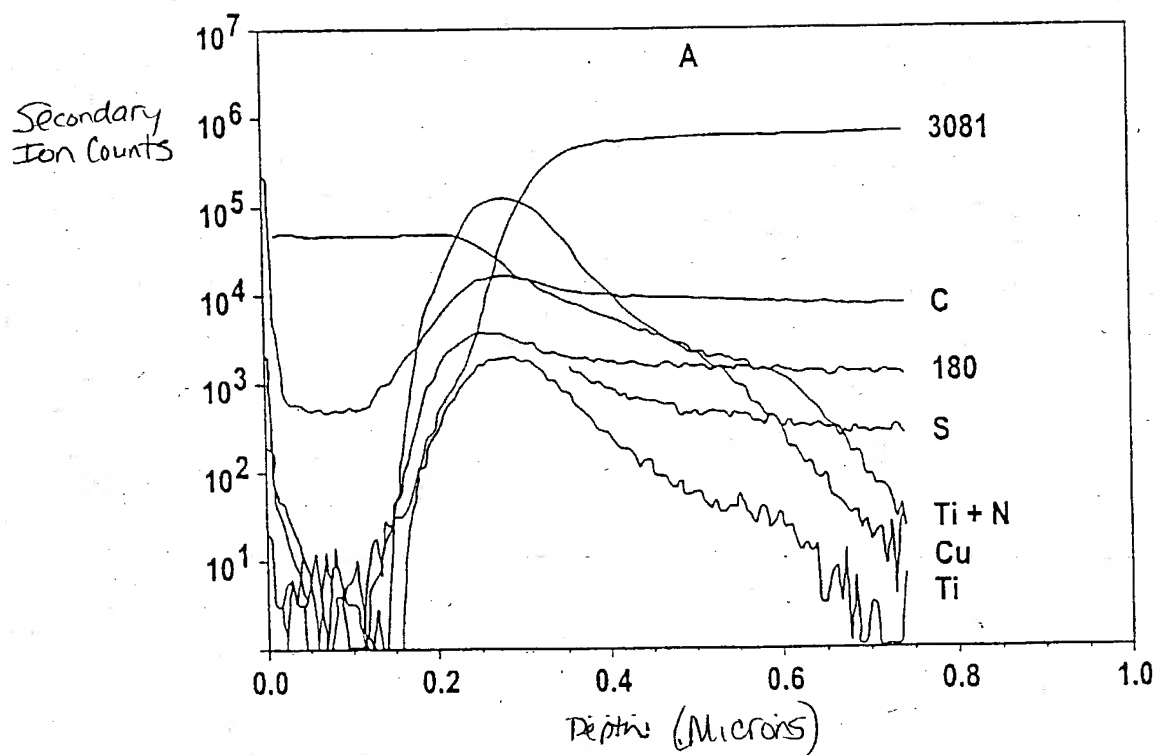


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Fig. 13a

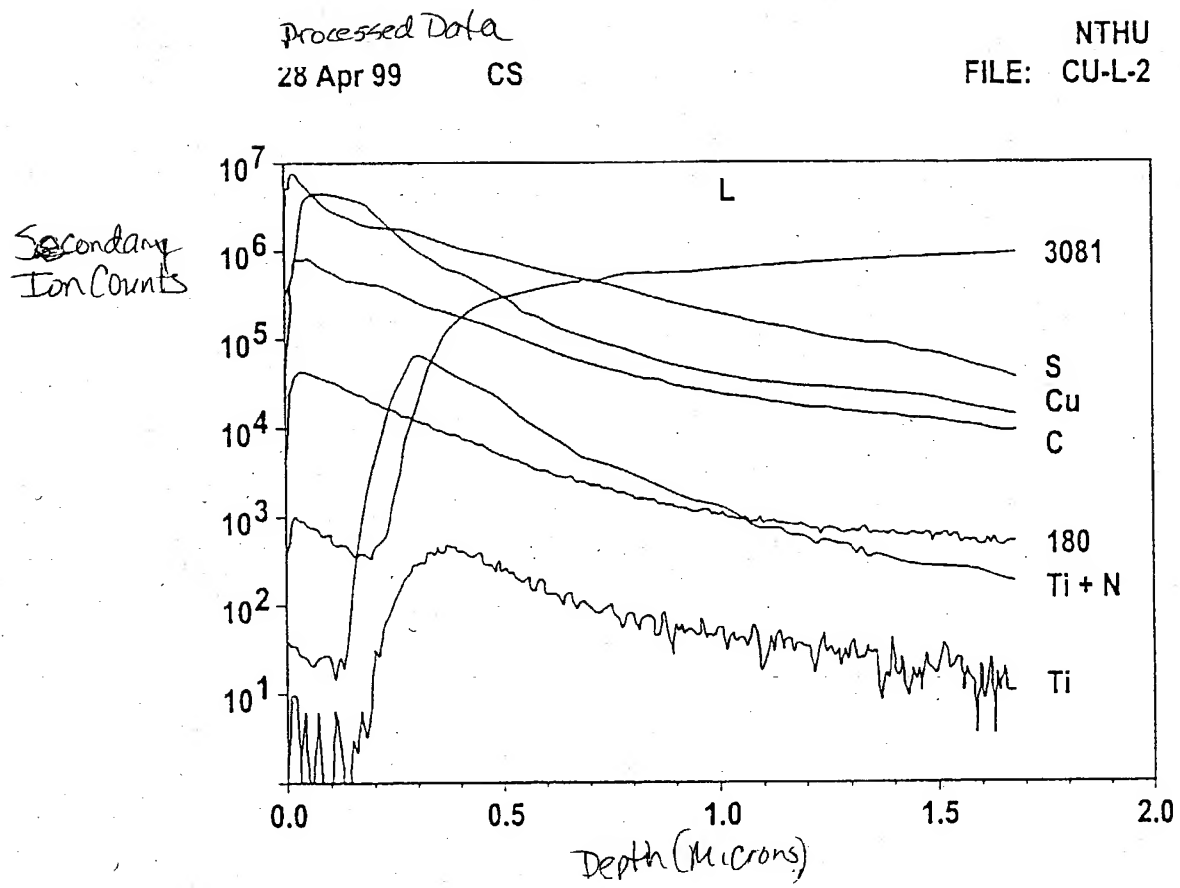
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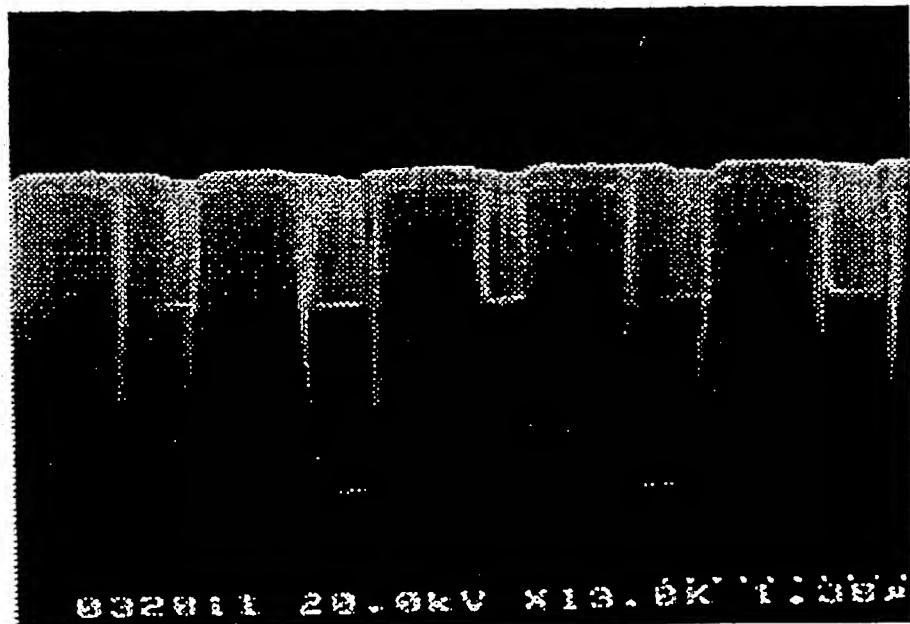
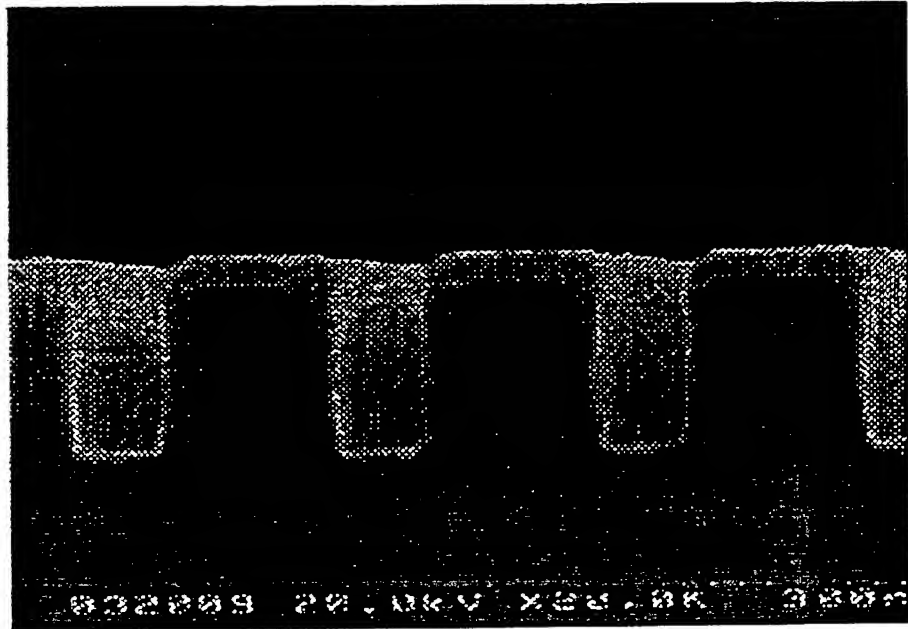
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Fig. 13b



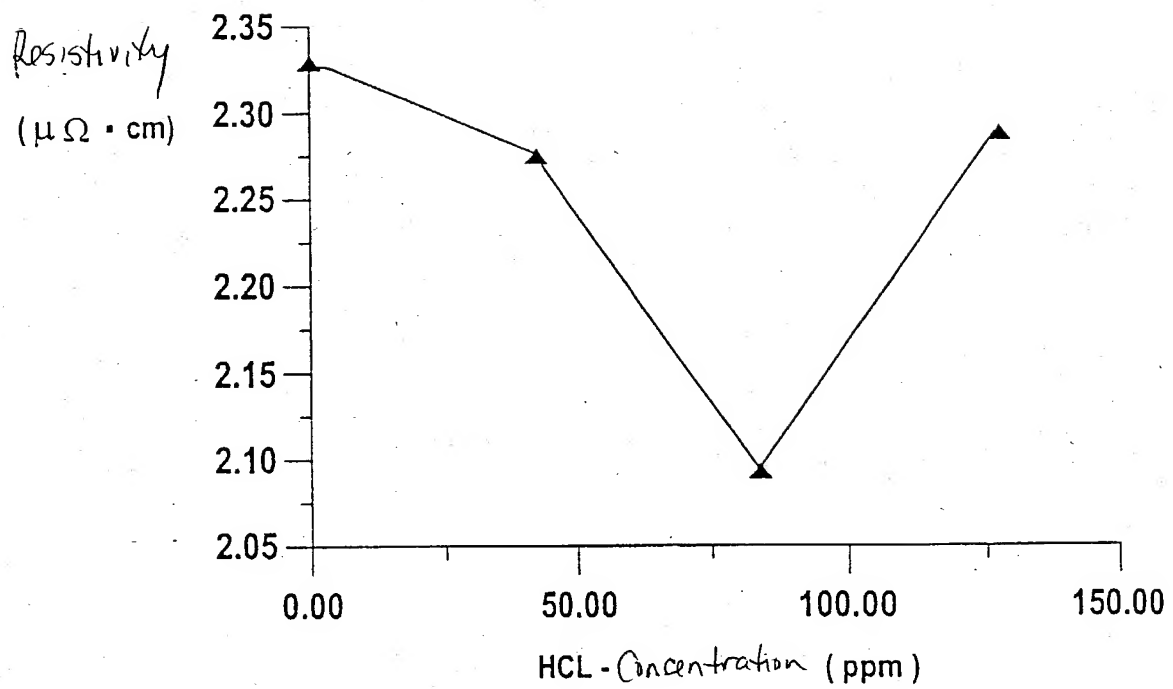
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Fig. 14



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Fig. 15



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Fig. 16a

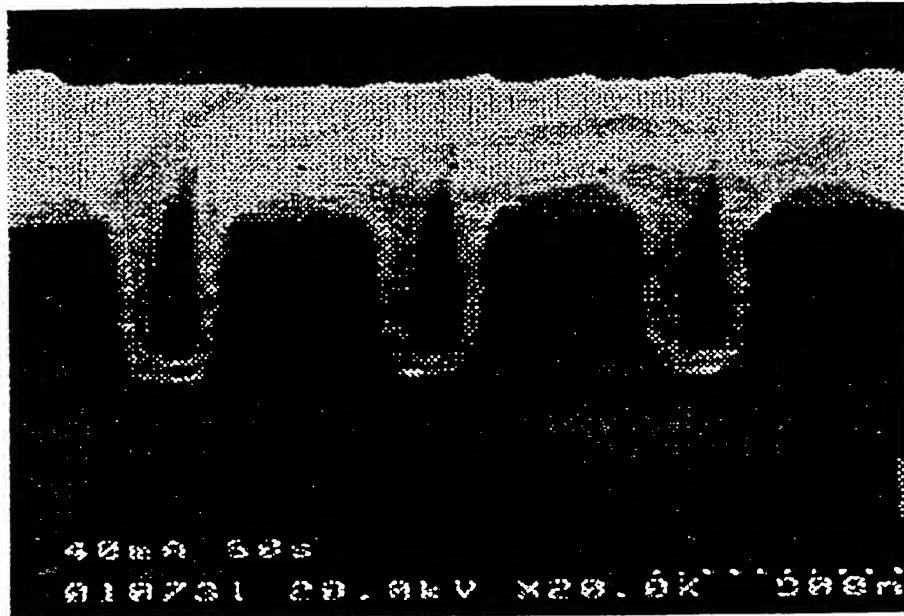
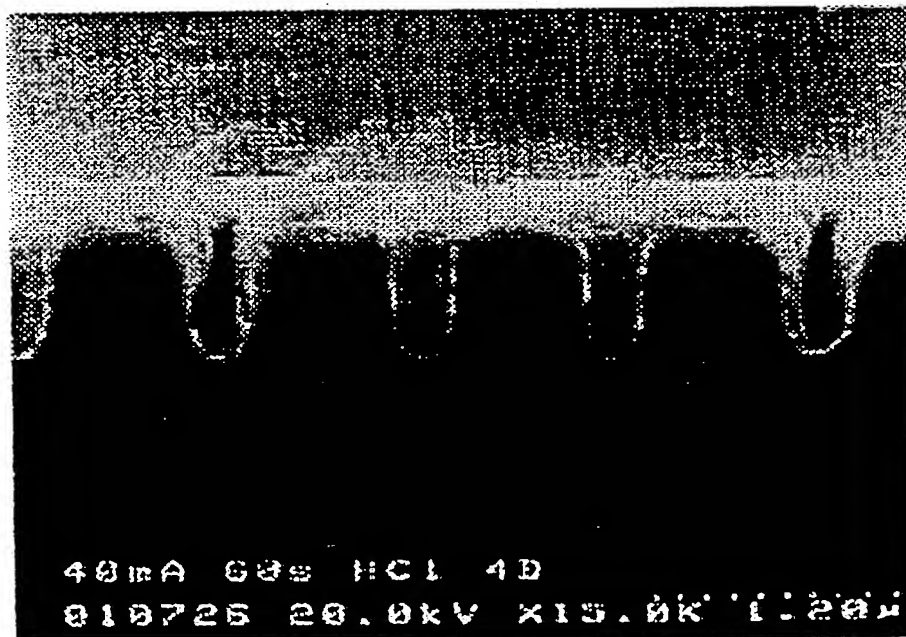
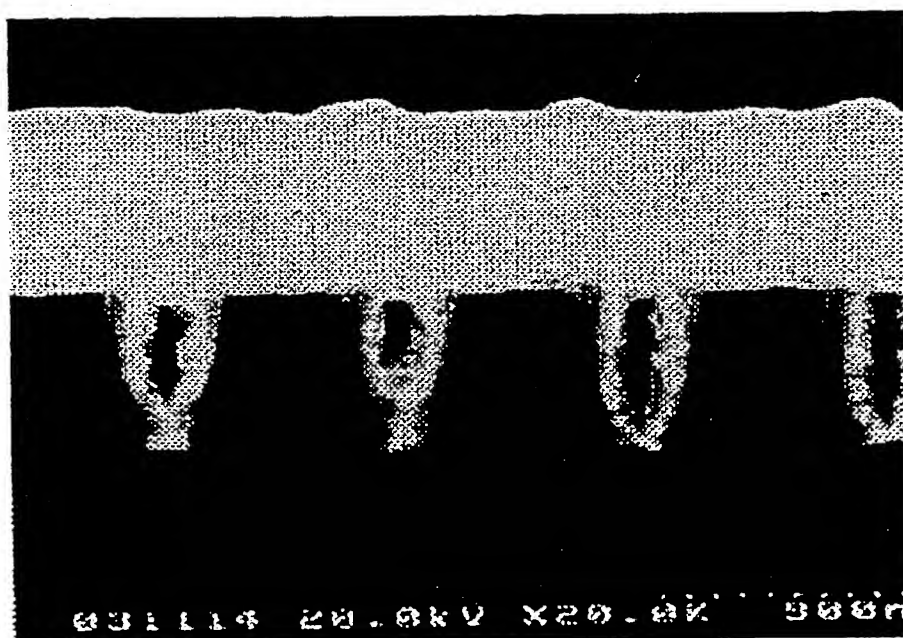
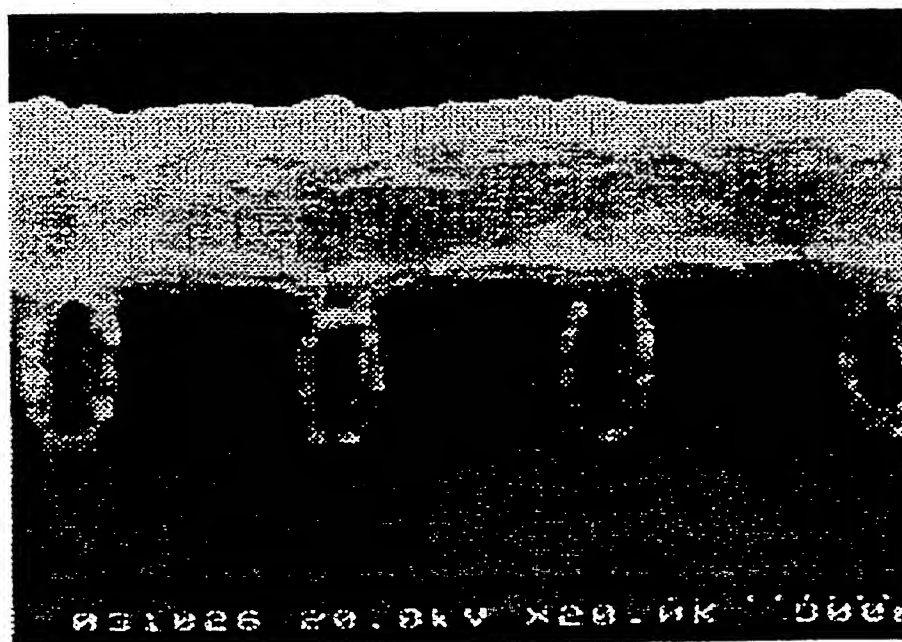


Fig. 16b



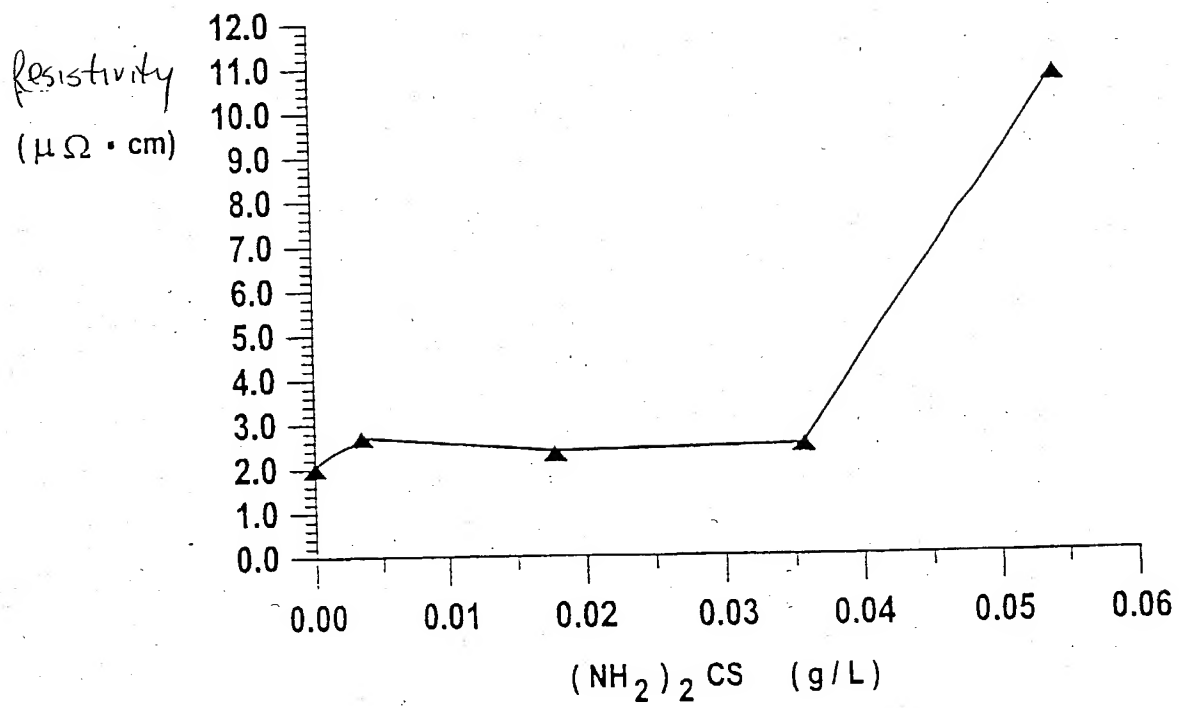
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Fig. 17



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Fig. 18



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Fig. 19

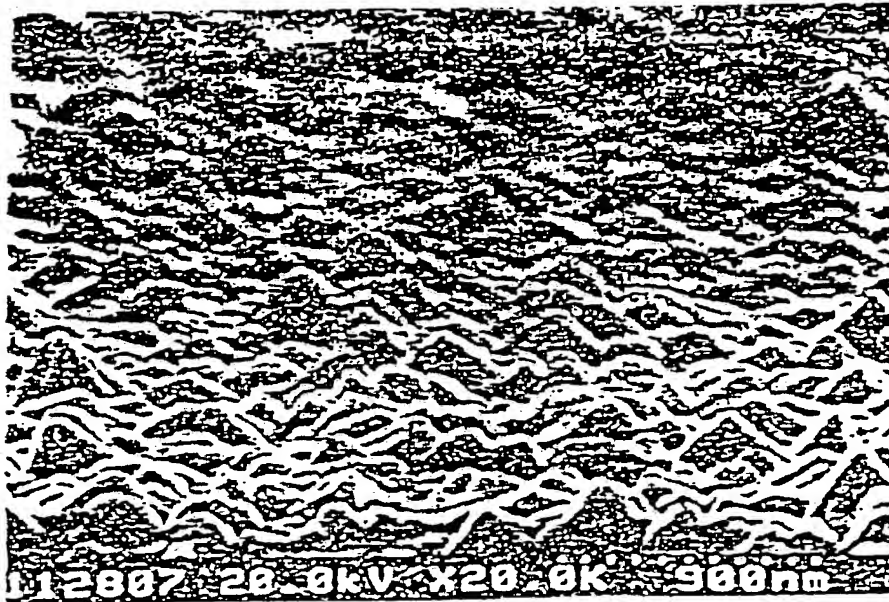
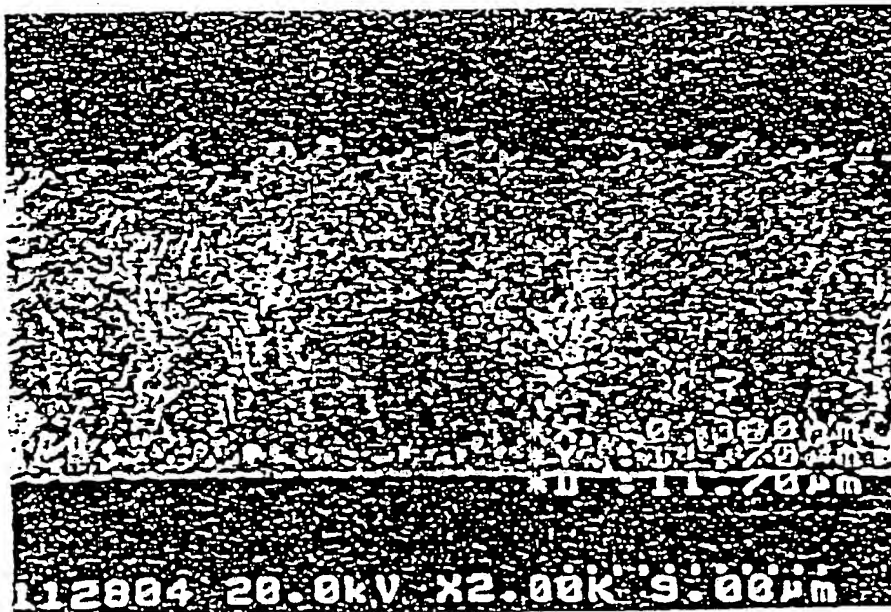
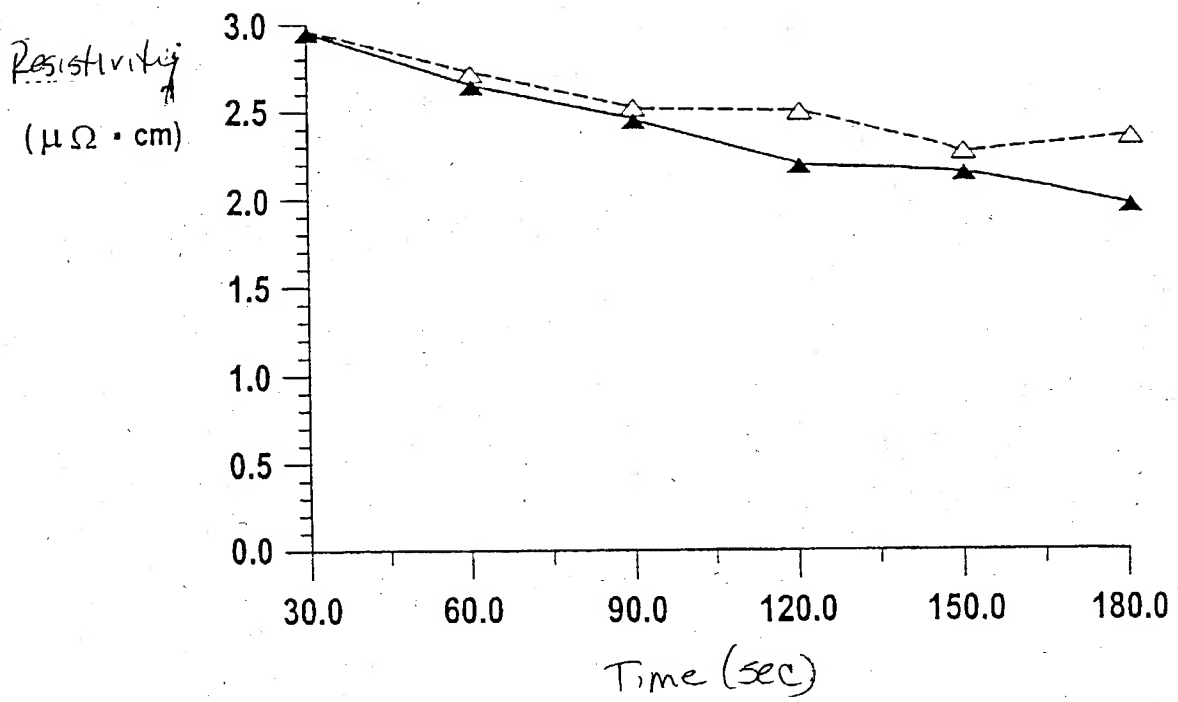


Fig. 20



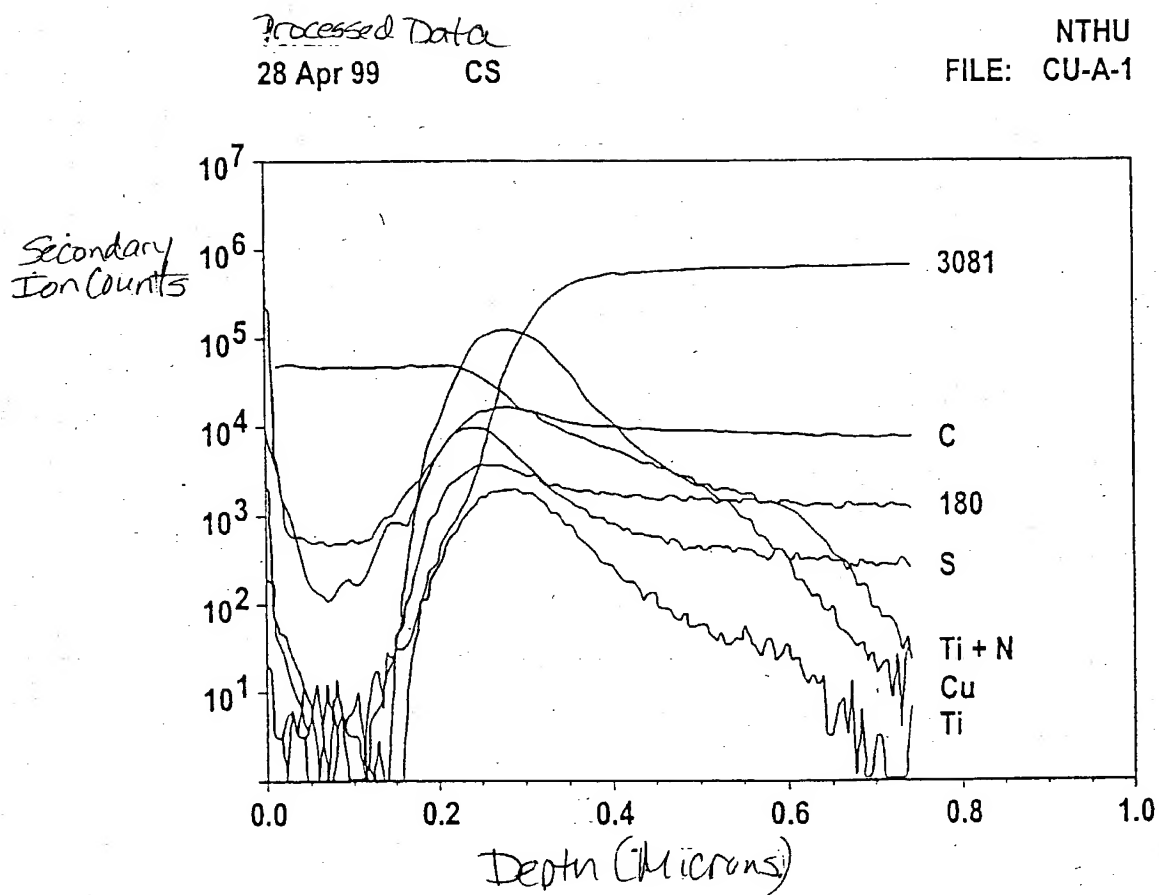
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Fig. 21



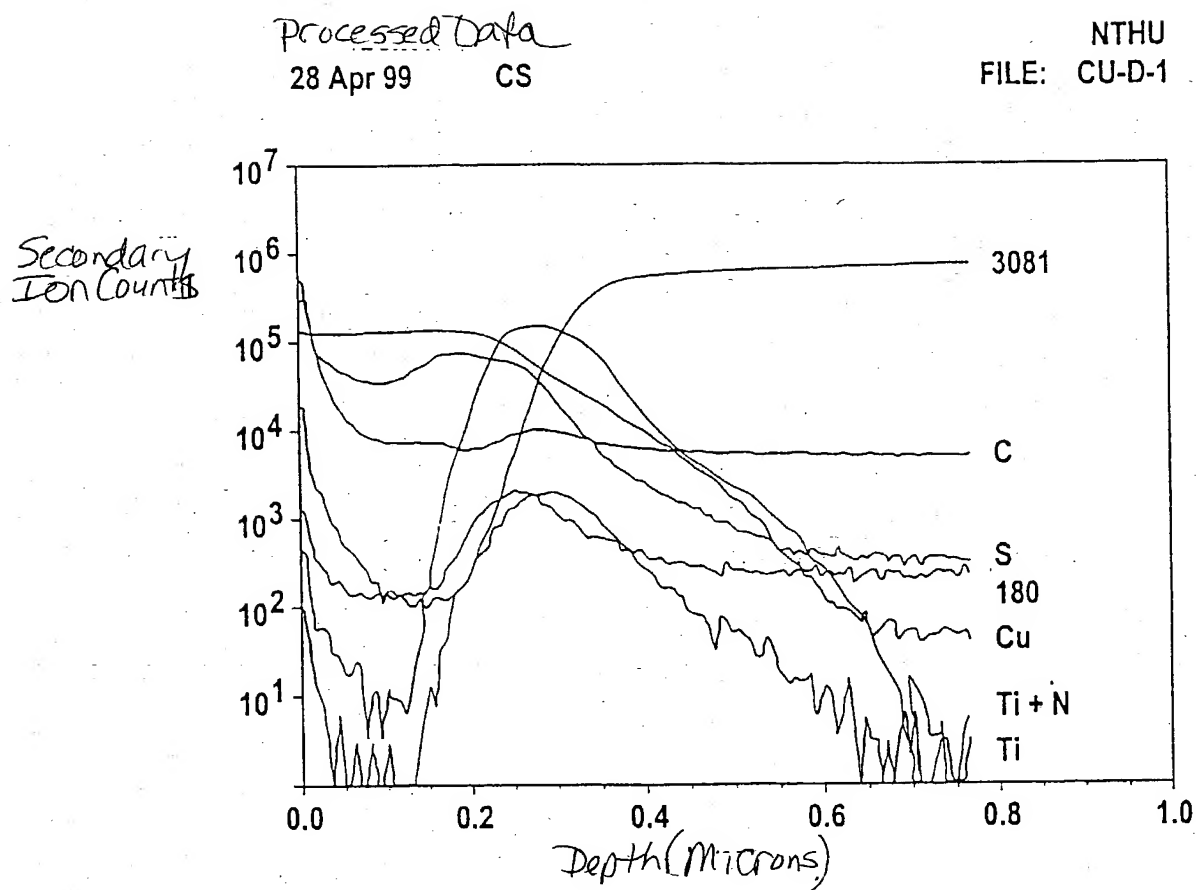
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Fig. 22a



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Fig. 22b



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Fig. 22c

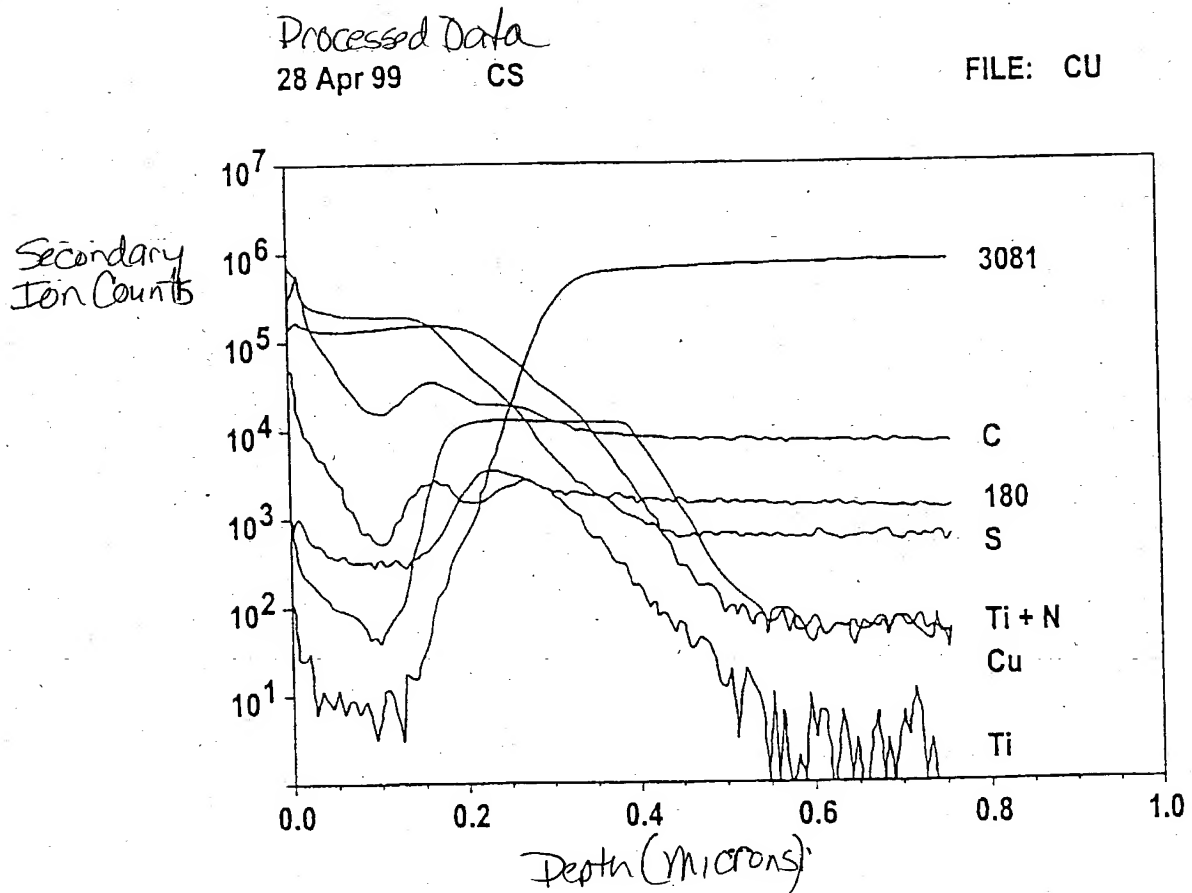
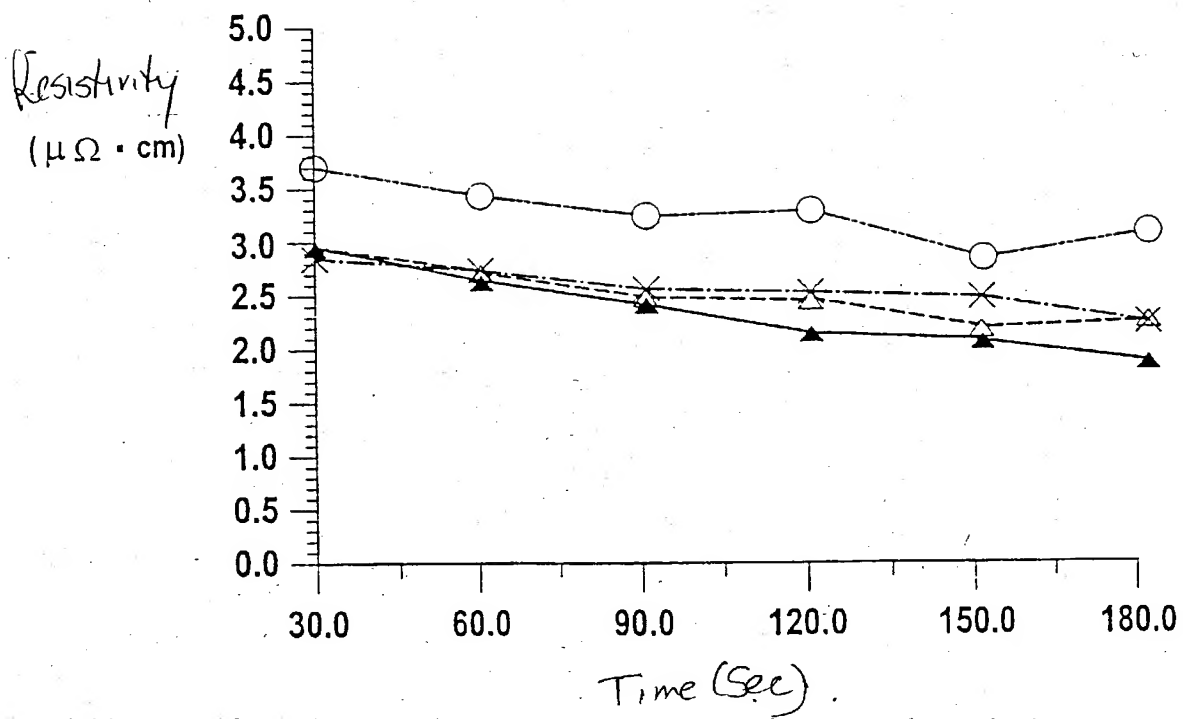


Fig. 23



- ▲ without additive agent
- △ 0,0036 g/L (NH₂)₂ CS und PEG200
- × 0,0036 g/L (NH₂)₂ CS und PEG1000
- 0,0036 g/L (NH₂)₂ CS und PEG4000

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Fig. 24a

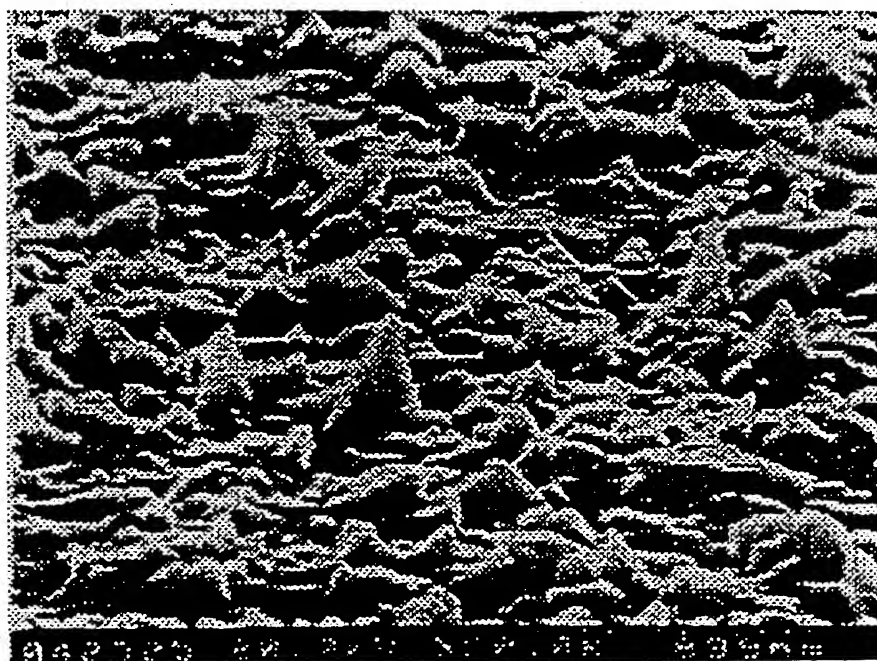
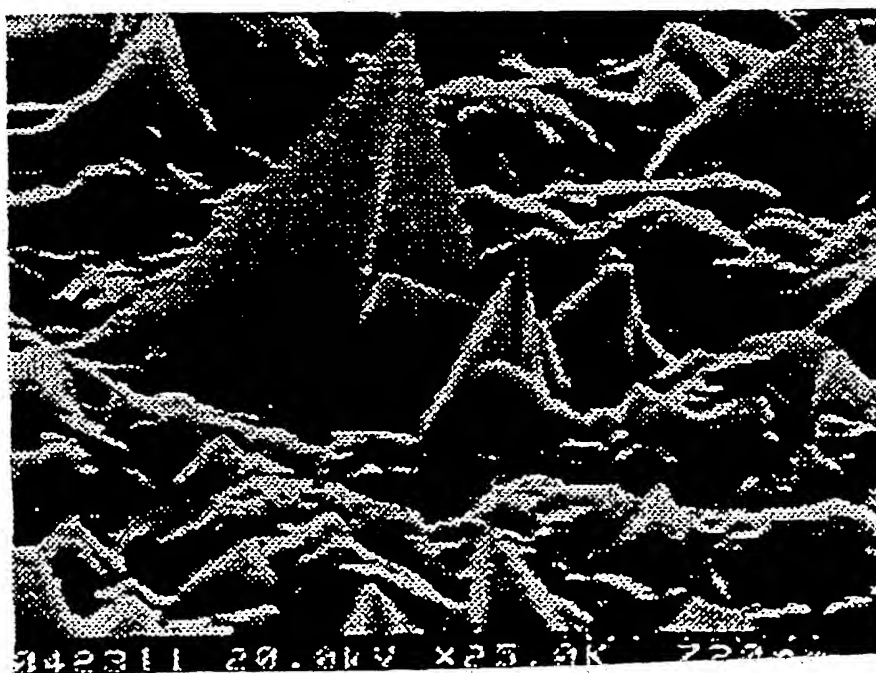
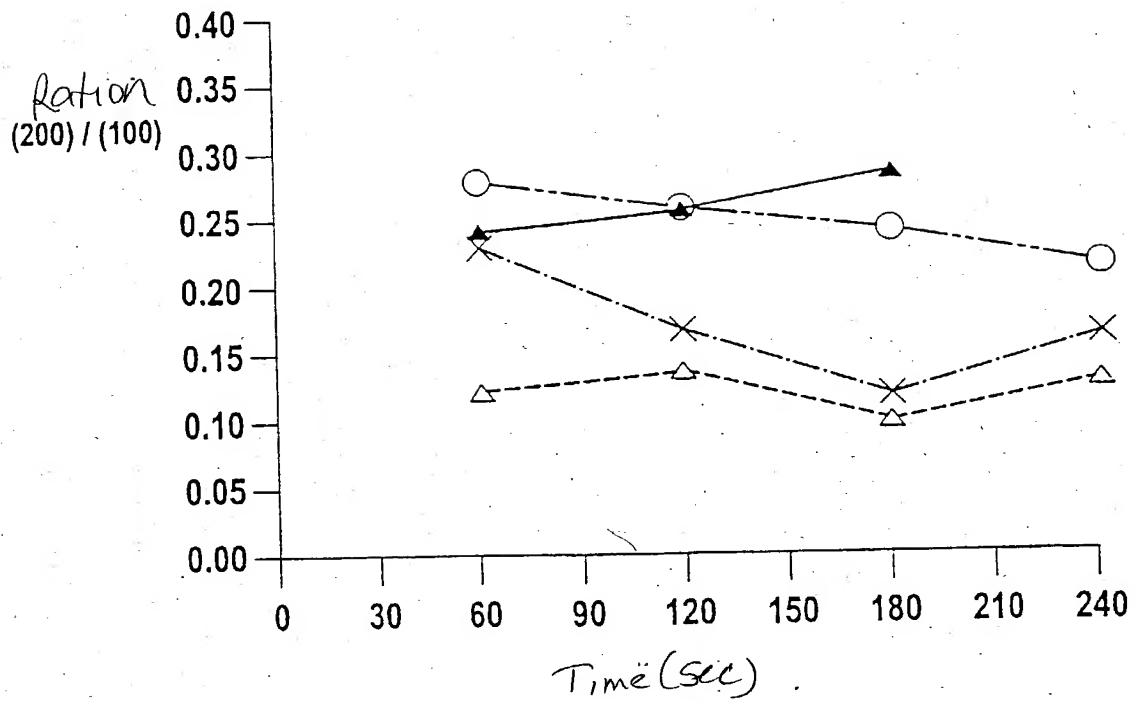


Fig. 24b



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Fig. 25

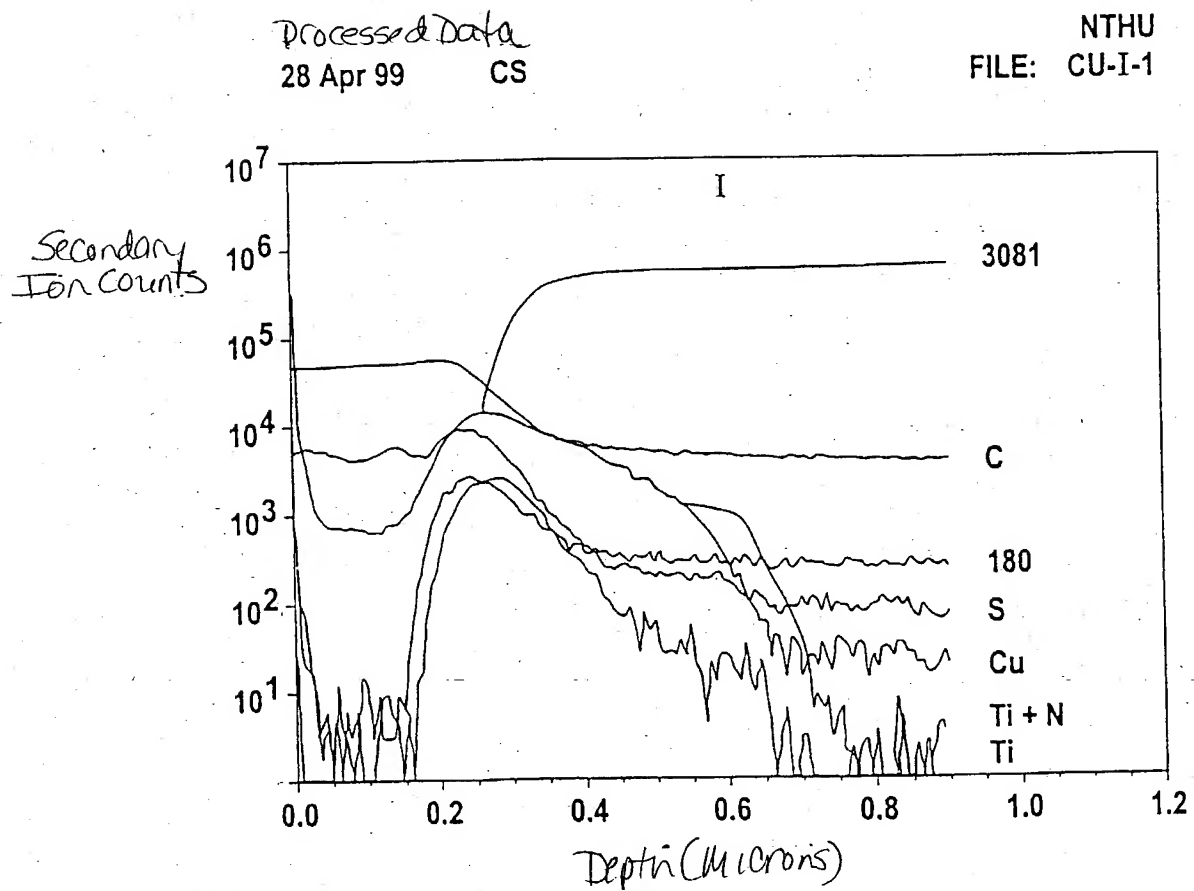


▲ S.T.D

△ (NH₂)₂CS + PEG200× (NH₂)₂CS + PEG1000○ (NH₂)₂CS + PEG4000

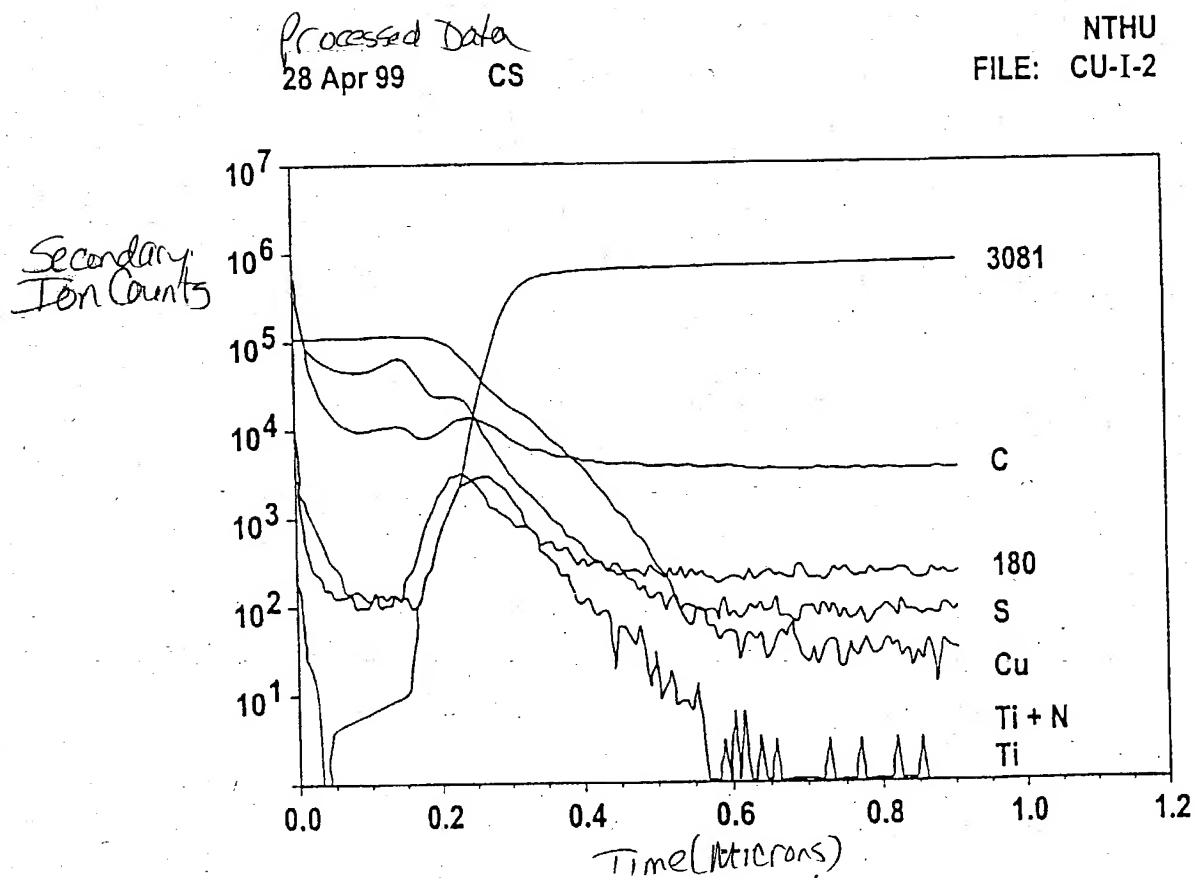
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Fig. 26a



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Fig. 26b



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Fig. 27

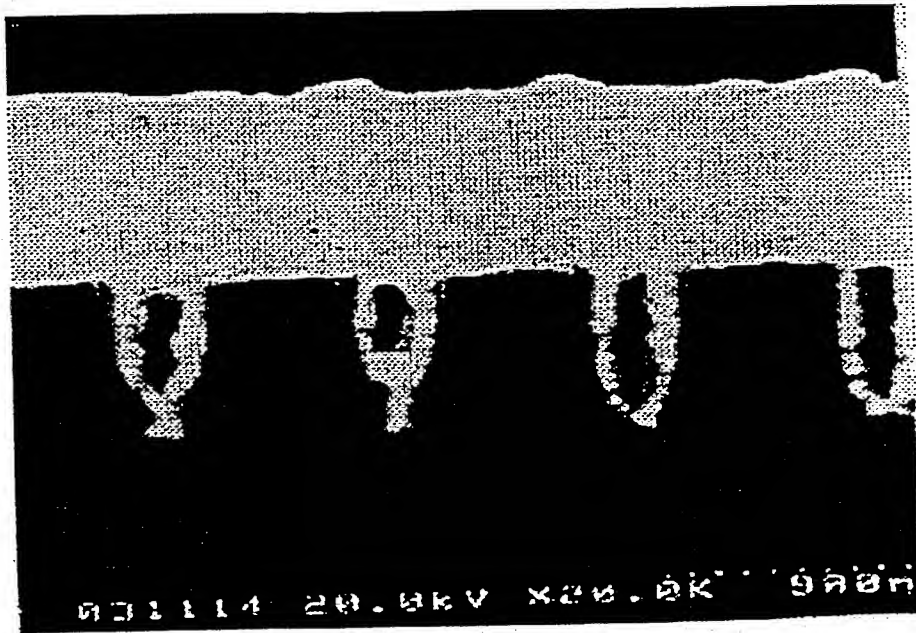


Fig. 28



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Fig. 29a

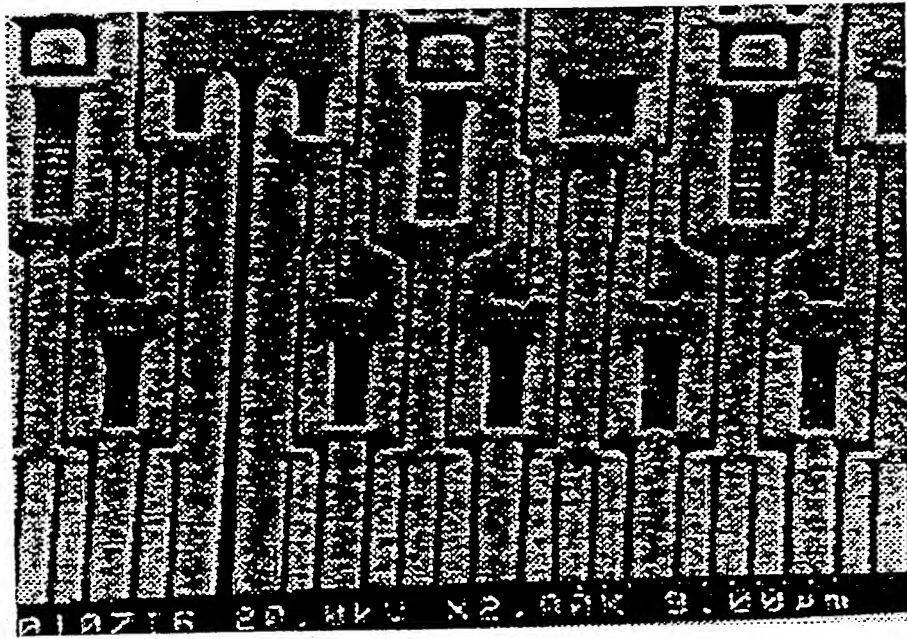
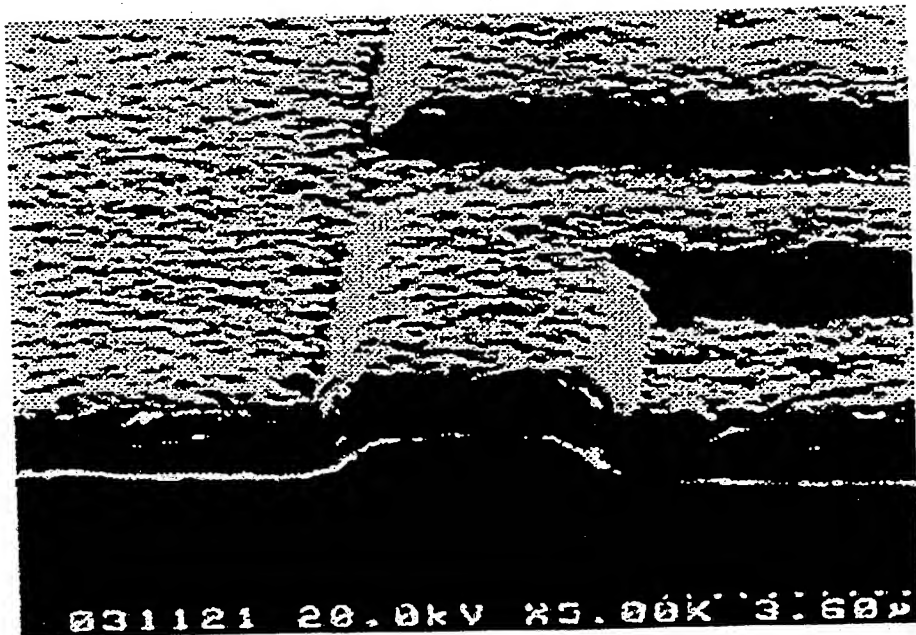
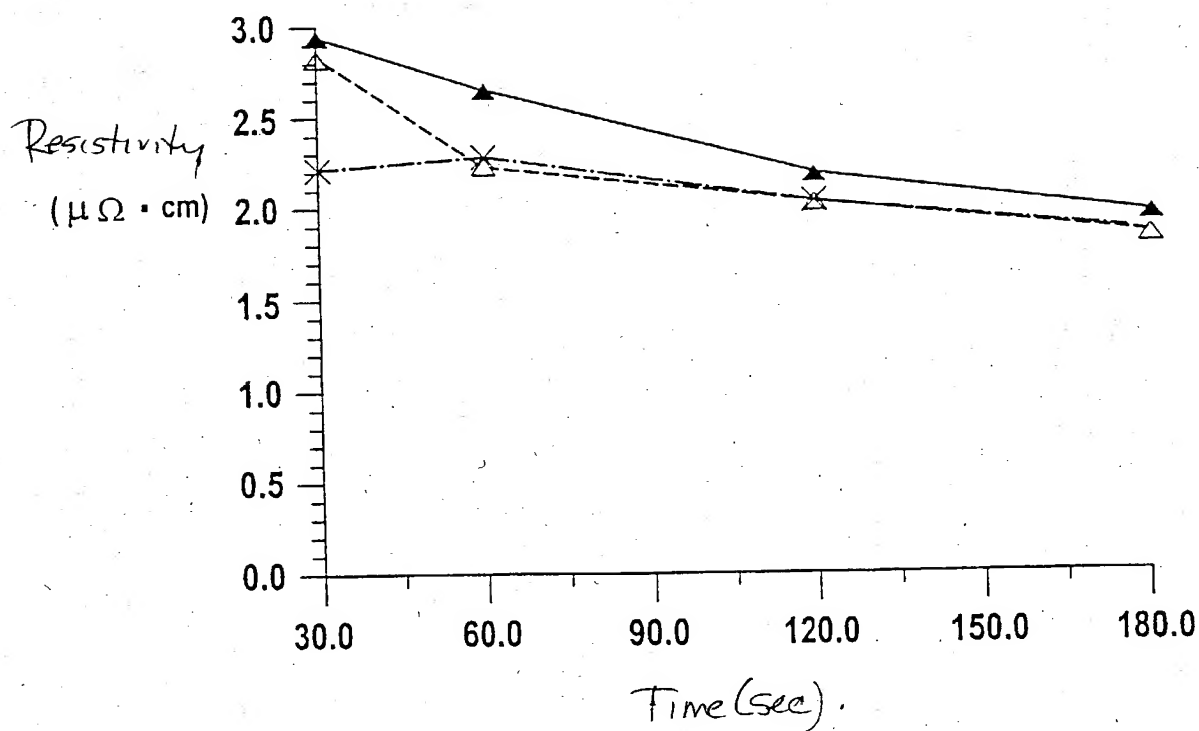


Fig. 29b



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Fig. 30

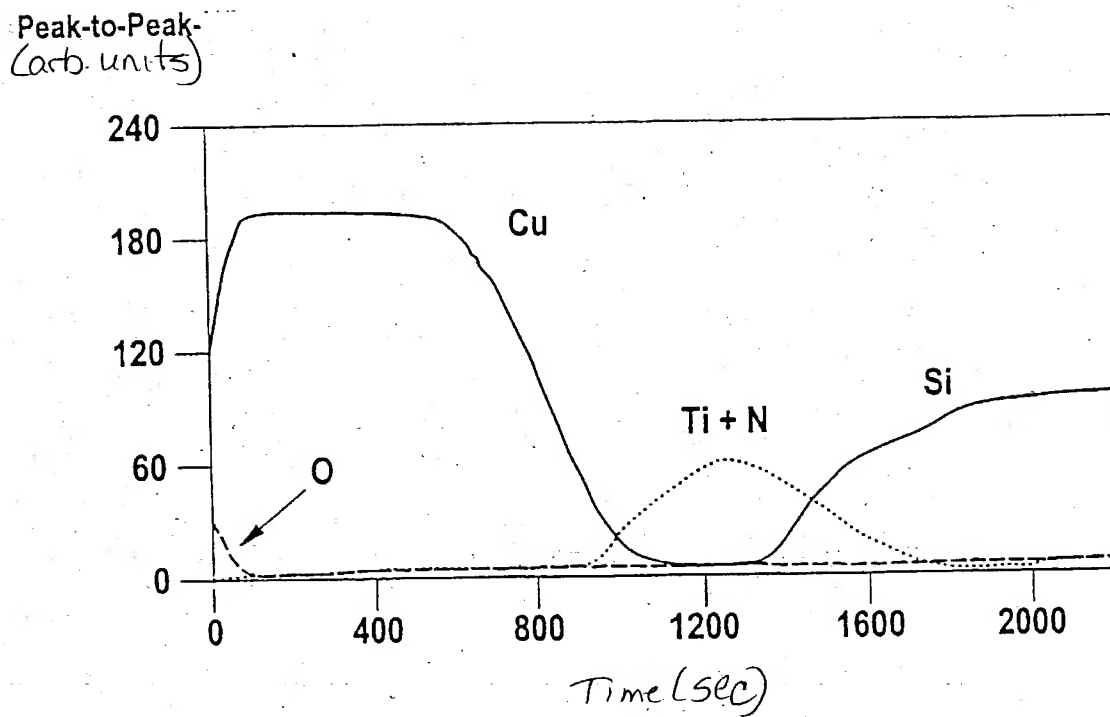


▲ without additive agent

△ with $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{SO}_4$ × with $\text{NH}_2\text{OH} \cdot \text{HCl}$

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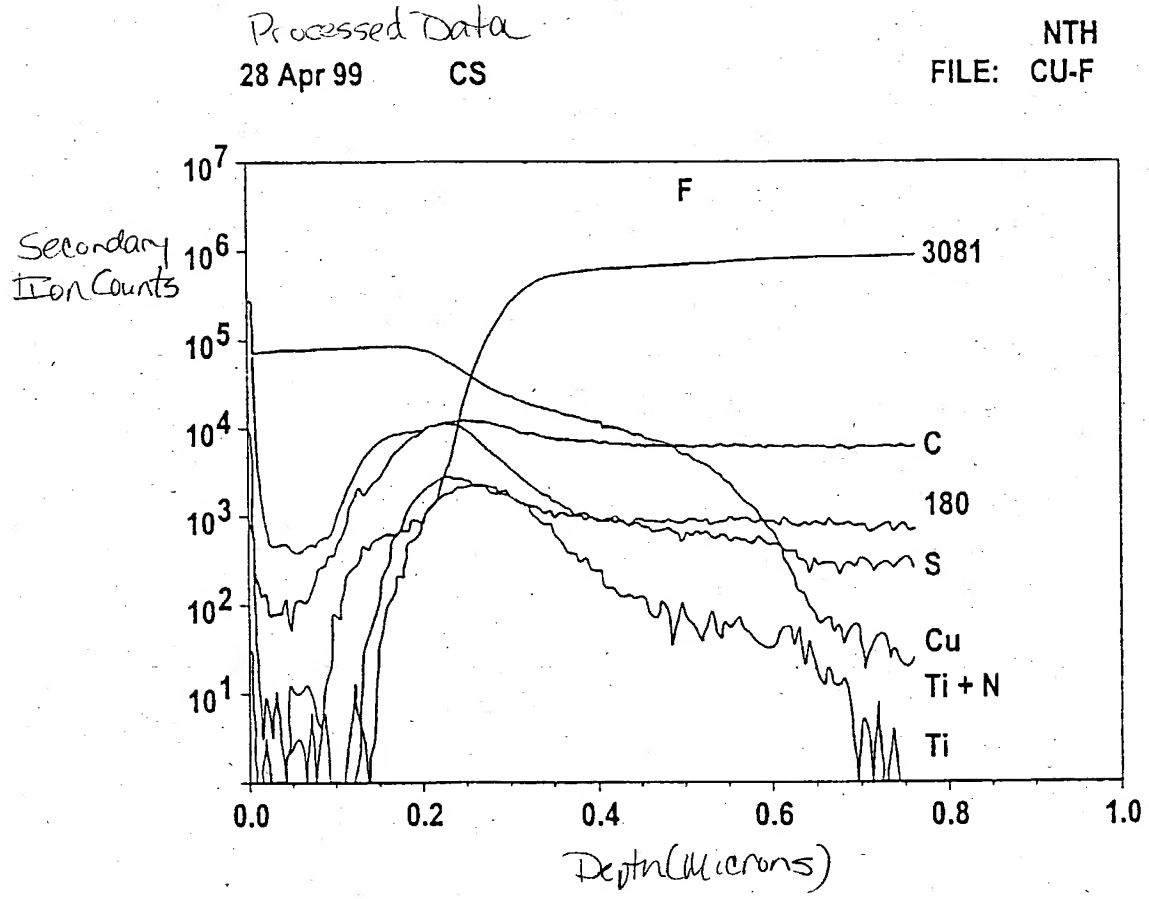
Fig. 31





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Fig. 32



COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (Includes Reference to PCT International Applications)			ATTORNEY'S DOCKET NUMBER MERCK-2395
<p>As a below named inventor, I hereby declare that:</p> <p>My residence, post office address and citizenship are as stated below next to my name.</p> <p>I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:</p> <p>ELECTROPLATING SOLUTION FOR COPPER ELECTROPLATING</p> <p>the specification of which (check only one item below):</p> <p><input type="checkbox"/> is attached hereto.</p> <p><input checked="" type="checkbox"/> was filed as United States application</p> <p style="margin-left: 40px;">Serial No. <u>10/070,000</u></p> <p style="margin-left: 40px;">on <u>1 MARCH 2002</u></p> <p style="margin-left: 40px;">and was amended</p> <p style="margin-left: 40px;">on ____ (if applicable).</p> <p><input checked="" type="checkbox"/> was filed as PCT international application</p> <p style="margin-left: 40px;">Number <u>PCT/EP00/08312</u></p> <p style="margin-left: 40px;">on <u>25 AUGUST 2000</u>,</p> <p style="margin-left: 40px;">and was amended under PCT Article 19</p> <p style="margin-left: 40px;">on ____ (if applicable).</p> <p>I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.</p> <p>I acknowledge the duty to disclose information which is material to patentability as defined in 37 CFR § 1.56, including for continuation-in-part applications, material information which became available between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.</p> <p>I hereby claim priority benefits under Title 35, United States Code, § 119 or 365 (b) of the following United States provisional application(s) and of any foreign application(s) for patent or inventor's certificate or 365(a) of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:</p>			
PRIOR U.S. PROVISIONAL AND FOREIGN/PCT APPLICATION(S) AND ANY PRIORITY CLAIMS UNDER 35 U.S.C. 119:			
COUNTRY (if PCT, indicate "PCT")	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED UNDER 35 USC 119
GERMANY	199 41 605.2	1 SEPTEMBER 1999	<input checked="" type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
POWER OF ATTORNEY: As a named inventor, I hereby appoint I. William Millen (19,544); John L. White (17,746); Anthony J. Zelano (27,969); Alan E.J. Branigan (20,565); John R. Moses (24,983); Harry B. Shubin (32,004); Brion P. Heaney (32,542); Richard J. Traverso (30,595); John A. Sopp (33,103); Richard M. Lebovitz (37,067); James E. Ruland (37,432); Jennifer J. Branigan (40,921); Robert E. McCarthy, (46,044); Csaba Henter (50,908) and Nicole E. Kinsey (50,723) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.			
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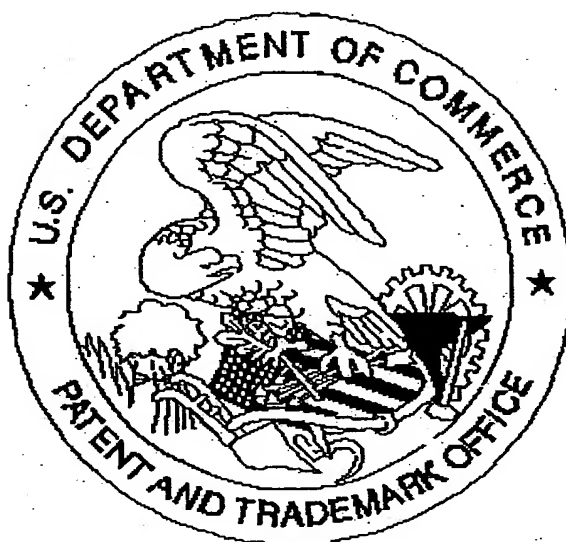
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SIGNATURE OF INVENTOR 201 <u>Hu Jung-chih</u>	DATE <u>2002-10-25</u>	SIGNATURE OF INVENTOR 207 <u>L. Ying-Huo</u>	DATE <u>23.10.02</u>
SIGNATURE OF INVENTOR 202 <u>Gau Wa-Chun</u>	DATE <u>Oct. 24 2002</u>	SIGNATURE OF INVENTOR 208 <u>Chen, Lih-Juann</u>	DATE <u>25.10.02</u>
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SIGNATURE OF INVENTOR 204 <u>Jeng Ming-Shian</u>	DATE <u>Oct. 23. 2002</u>	SIGNATURE OF INVENTOR 210	DATE
SIGNATURE OF INVENTOR 205 <u>CHENG Chun-Lin</u>	DATE <u>Oct. 28. 2002</u>	SIGNATURE OF INVENTOR 211	DATE
SIGNATURE OF INVENTOR 206 <u>Lin You-Shin</u>	DATE <u>Oct. 30. 2002</u>	SIGNATURE OF INVENTOR 212	DATE

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